



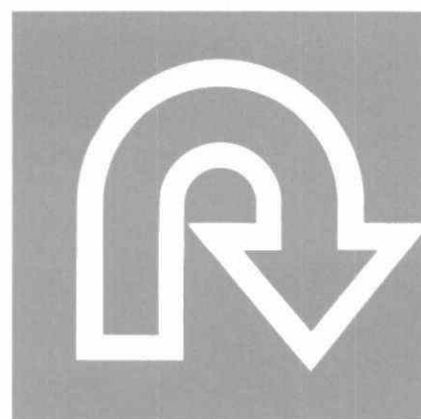
**FEDERAL/PROVINCIAL  
RESEARCH AND MONITORING  
COORDINATING COMMITTEE (RMCC)**

**ASSESSMENT OF THE STATE  
OF KNOWLEDGE  
ON THE LONG-RANGE  
TRANSPORT  
OF AIR POLLUTANTS  
AND ACID DEPOSITION**

**PART 2  
ATMOSPHERIC SCIENCES**

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MOE**

**AUGUST 1986**



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part 2

Assessment of the state of  
knowledge on the long-range  
transport of air pollutants and  
acid deposition.

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FEDERAL/PROVINCIAL RESEARCH AND  
MONITORING COORDINATING COMMITTEE (RMCC)

ASSESSMENT OF THE STATE OF KNOWLEDGE  
ON THE LONG-RANGE TRANSPORT  
OF AIR POLLUTANTS AND ACID DEPOSITION

**PART 2**  
**ATMOSPHERIC SCIENCES**

RMCC ATMOSPHERIC SCIENCES SUBGROUP

AUGUST 1986



PREFACE

In the fall of 1984, the Federal/Provincial Acid Rain Research and Monitoring Co-ordinating Committee (RMCC) decided to undertake an assessment of the state of knowledge on the long-range transport of airborne pollutants and acid rain gained since the MOI publications in 1982. The Atmospheric Sciences Sub-group (ASSG) of the RMCC was given the task of assembling a team of scientists to prepare the portion of the assessment dealing with the atmospheric sciences.

After several iterations a series of five questions, many having a direct relevance to acid rain policy implementation, were formulated as indicated in the following Executive Summary.

In order to answer these questions the report was organized with chapters in the same sequence as the questions, addressing each of the topics under appropriate sub-headings. The last question can be addressed using either observations or models and so two chapters were devoted to this. An overall summary of the report is given in the Executive Summary.

The author(s) are indicated, with the group leader first, as a footnote at the bottom of the first page of each chapter/section. All chapters were reviewed by other team members. A complete listing of the assessment team is given in Appendix 2-A. The RMCC/ASSG co-chairmen wish to acknowledge the efforts of the assessment team, especially the group leaders, for their contributions to the report, and the ASSG members for their helpful comments.

P.W. Summers and M. Lusiš  
Editors  
Co-chairmen Atmospheric Science Subgroup

ENTERED MAY 25 2001

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## EXECUTIVE SUMMARY

### Question 1

**What are the present emissions of acidifying pollutants in North America?**

- The most complete picture of the emissions of SO<sub>2</sub> and NO<sub>x</sub> currently available is for the base year 1980.
- The 1980 U.S. emissions of SO<sub>2</sub> are estimated at 24 million tonnes, with thermal power generation contributing about two-thirds of the total. Canadian emissions amount to 4.6 million tonnes, slightly less than one-half of the total coming from the non-ferrous smelting sector. About 80% of the total emissions come from the 31 states east of the Mississippi River and the provinces east of the Manitoba-Saskatchewan border.
- The 1980 emissions of NO<sub>x</sub> are estimated at 21 and 1.7 million tonnes in the U.S. and Canada respectively, with transportation and power generation being the most important contributors. The emissions of NO<sub>x</sub> are more evenly distributed than those of SO<sub>2</sub>, although the eastern parts of both countries are each responsible for more than 60% of the emissions.
- The estimated errors of the SO<sub>2</sub> and NO<sub>x</sub> emissions inventories on a national basis are less than 10%. On a regional basis the errors may be higher.
- The seasonal variations in sulfur and nitrogen oxide emissions is relatively small - estimated to be less than  $\pm 10\%$  from the annual average.
- The acid-forming potential of anthropogenic sulfur oxide emissions in eastern North American is currently approximately twice that of nitrogen oxide emissions.
- Natural emissions of sulfur and nitrogen oxides still have a considerable degree of uncertainty, but in eastern North America even upper-limit estimates are small compared to anthropogenic emissions.
- Work is underway on, and preliminary data are available for, the emissions of other substances involved in the chemistry of acid rain formation (alkaline materials, photochemically active hydrocarbons), but the values are highly uncertain.

### Question 2

**How have emissions changed during the past 30 years?**

- Emissions of SO<sub>2</sub> in the U.S. rose from close to 20 million tonnes in

1950 to 28 million tonnes in 1970, before dropping to 24 million tonnes in 1980. In the midwestern states, SO<sub>2</sub> emission levels peaked in the mid-60's, but 1980 levels were still about 25% higher than in the early 1950's.

- Canadian SO<sub>2</sub> emissions increased from 4.5 million tonnes in the mid-1950's to 6.7 million tonnes in the late 1960's, but by 1980 had dropped to 4.6 million tonnes. Eastern Canada contributed the bulk of these emissions.
- Recent estimates indicate that the decline in SO<sub>2</sub> emissions accelerated from 1979 to 1982, in part due to the economic recession. There is also an indication that SO<sub>2</sub> emissions may have increased again slightly in 1983 in response to the economic recovery. Such short-term departures, from longer term trends due to emission control implementation, are expected to continue in response to the level of economic activity.
- Changes in the geographical location of sources are not well documented. In the NE portion of North America there has been some redistribution of SO<sub>2</sub> emissions from small urban sources to large (power plant) rural sources. There has been a major shift in the U.S. population to the southern States and with it an increase in the southern emissions which may continue.
- Emissions of NO<sub>x</sub> in the U.S. have increased significantly in all areas, from about 9 million tonnes in 1950 to 21 million tonnes in 1980. The increase ranged from a factor of two in the northeast to over three in the south. Canadian NO<sub>x</sub> emissions have also more than doubled since the early 1950's, from 0.6 million tonnes in 1955 to 1.7 million tonnes in 1980, but their geographical distribution has remained approximately the same.
- There have also been changes in the characteristics of the emission sources. There has been a progressive increase in the proportion of SO<sub>2</sub> released from tall stacks, for example, enhancing the potential for long-range transport of this gas. Similarly, particulate control devices, which are currently widely used, have tended to remove a large portion of the alkaline particulates which were previously emitted to the atmosphere, but the implications of this on the acid rain problem are unclear.

### Question 3

#### **What are present regional-scale concentration/deposition patterns?**

- The concentration/deposition patterns for the major species contributing to precipitation acidity in eastern North America are now better defined than in 1980 but show no significant overall change in either spatial distribution or intensity.

- Most of the U.S. east of the Mississippi Valley (with the exceptions of the extreme SE and around Lake Superior) receives a wet deposition loading of  $\text{SO}_4^{=}$  in excess of  $20 \text{ kg ha}^{-1} \text{ yr}^{-1}$ .
- Southern and central Ontario and southern Québec also have a wet loading in excess of  $20 \text{ kg ha}^{-1} \text{ yr}^{-1}$  in all recent years although the boundary of this area varies by a few hundred km from year to year.
- In the Atlantic Provinces the wet deposition of  $\text{SO}_4^{=}$  is close to  $20 \text{ kg ha}^{-1} \text{ yr}^{-1}$ , the value being slightly exceeded in some places in some years and not in others.
- In the west, the pH is generally well above 5.0 except for some smaller regions around the main population centres (i.e. the Los Angeles basin, the San Francisco basin and the Seattle-Vancouver area). Because of the very complex terrain, and highly variable precipitation, the geographic loading patterns are not yet well defined but appear to be still below  $20 \text{ kg ha}^{-1} \text{ yr}^{-1}$  wet  $\text{SO}_4^{=}$ .
- With the addition of several years of new data some interesting new aspects of wet deposition are now well documented:
  - (a) there is a strong annual cycle in the region of heavy deposition in the NE U.S. and SE Canada. The deposition of acidity ( $\text{H}^+$ ) and  $\text{SO}_4^{=}$  maximizes in the late Summer and Fall; the deposition of neutralizing substances such as  $\text{Ca}^{++}$  maximizes in the Spring and for  $\text{NH}_4^+$  in the Fall.
  - (b)  $\text{NO}_3^-$  deposition is more constant through the year and thus potentially contributes relatively more to the acidity of winter snow than to summer rain (in some places around the lower Great Lakes and in New England  $\text{NO}_3^-$  has the potential to contribute more on an absolute basis than  $\text{SO}_4^{=}$  to snowfall acidity).
  - (c) wet deposition of both  $\text{SO}_4^{=}$  and  $\text{NO}_3^-$  is highly episodic with more than 50% of the annual deposition at stations in eastern Canada occurring in only 20% of the precipitation events.
- Dry deposition can be estimated from limited air concentration measurements and budget studies. Routine daily air concentration measurements have been made in Canada at a small number of rural sites since 1980; they are just now commencing in the U.S.A. Indications are that:
  - (a) over eastern North America as a whole, dry and wet deposition of S and N oxides are approximately equal.
  - (b) closer to the major source regions dry deposition tends to exceed wet.
  - (c) in more remote areas (i.e. most of eastern Canada) dry accounts for only about 20% of the total deposition.

(d) dry deposition is also highly episodic with only 20% of the days in a year accounting for over 50% of the annual dry deposition.

- There is increasing evidence that wet deposition from the direct impact of fog and/or low clouds, to high elevation forests in eastern North America, can provide a deposition rate equivalent in magnitude to that from either precipitation or dry deposition alone.
- A comparison of eastern North American and European air and precipitation quality data shows comparable levels of precipitation acidity (long-term pH about 4.1 at the centre of the impacted region), but higher levels of sulfates in central and eastern Europe than in eastern North America. Nevertheless, much of eastern North America (east of the Mississippi River) receives sulfate wet deposition levels comparable to those currently observed in southern Scandinavia. Nitrates play an important role in the precipitation chemistry of both continents. Airborne concentrations of sulfur oxides are greater in central Europe than eastern North America, and short-term elevated values are more common there. The frequency of occurrence of elevated ozone levels is comparable in portions of the eastern United States and Europe.

#### Question 4

**Have these patterns changed during the past 30 years?**

- In North America, reliable wet deposition data are available, for the most part, only since about 1980. The European observations go back somewhat longer. Due to the lack of a long-term record, and changes in sampling methodology, conclusions regarding trends over the past 30 years are somewhat tenuous.
- However, monitoring in remote parts of the world has shown that sulfate and nitrate concentrations in industrialized areas of Europe and North America are greater by at least a factor of five, indicating that due to anthropogenic emissions, levels in these industrialized areas have increased by this amount since sometime prior to the 1950's.
- Recent trend analysis of the European precipitation data since the 1950's has suggested a reasonable correspondence between emissions and deposition, with precipitation sulfate concentration changes at most Scandinavian stations generally following the estimated emissions changes in several of the countries known to contribute significantly to deposition in Scandinavia.
- Precipitation is currently more acidic in parts of the eastern United States, particularly the southeast, than it was in the mid-1950's or mid-1960's. The more reliable data over the five years ending in 1984 suggest a slight decrease in precipitation concentrations and wet deposition of sulfates in eastern North America. Thorough analyses to establish the cause of these changes have not been conducted so far.



- Visibility has been suggested as a surrogate measure for the atmospheric boundary layer loading of acidifying airborne substances such as sulfates. However, due to limitations in the data set, it is not possible to carry out analyses of trends in regional visibility patterns with any degree of confidence.

#### Question 5

**How well can we estimate concentration/deposition fields from source-receptor (S-R) relationships?**

- The answer to this question depends on the relevant temporal and spatial scales and the level of detail required. No major breakthroughs have been made since 1980 but, the continued accumulation and interpretation of data and modelling developments are slowly increasing the precision with which this question can be answered.
- On a global scale there is a strong geographical association between the regions of highest emissions and of maximum wet deposition/acidity.
- Remote area monitoring and theoretical studies indicate global background wet deposition levels of  $1-3 \text{ kg ha}^{-1} \text{ SO}_4$  per year (with associated pH of about 5.0). Deposition values in northeastern North America are up to 16 times greater (over the lower Great Lakes) than this, clearly slowing the link with man-made emissions.
- At individual stations, daily measurements of air and precipitation  $\text{SO}_4$  and  $\text{NO}_3$  concentrations show strong variations with the direction of arrival of air parcels. Stratification of concentration observations by broad wind sectors indicates high correlation between the emissions within a sector and the observed values: however, the contributions from nearby or more distant sources cannot be distinguished.
- Estimates of fluxes of S and N from North America into the North Atlantic (approximately 30% of the emissions) are consistent with earlier budget estimates. From these and modelling estimates the simple source-receptor relationship of approximately 50% of the S deposition in Canada resulting from U.S. emissions and approximately 50% from Canadian emissions, has been established. Apportionment of nitrogen species is less certain but appears to behave similarly to S.
- The numerical models applied in the Memorandum of Intent (MOI) reports of 1982 were criticized in a number of areas, such as their assumptions that the chemistry is linear, their simplistic treatment of atmospheric transport, and their ignoring of topographical changes and diurnal variability. A considerable amount of additional work has been done since the MOI studies to evaluate these relatively simple long-range transport (LRT) models, which indicates that wet deposition of sulfur over a one-year period is reasonably well simulated (to better than within a factor-of-two of the observations), and that on this time

scale the non-linear effects of sulfur chemistry are not critical (some of the monitoring data also support this conclusion). Thus the simple models can now be more confidently used for (current) source-receptor relationship studies for sulfur deposition. The uncertainties in the model source-receptor relationships require further investigation.

- A large-scale experiment with inert tracer gas releases from Ohio and Sudbury showed that simple, linear trajectory LRT models can perform well under selected meteorological situations in simulating the tracer transport and thus provided additional confidence in the use of the models as qualitative tools for estimating source-receptor relationships.
- The use of trace elements in the atmosphere (tracers of opportunity), associated with large regions to act as markers for air masses (and hence man-made pollution origin), is a rapidly developing new approach. First results from this approach are qualitatively consistent with the Lagrangian modelling results, but the technique needs more experimental testing.
- Several Eulerian long-range transport models have now been developed which include a state-of-the-art treatment of atmospheric transport, transformation and deposition processes, thus in large part addressing the earlier criticisms levelled at the simple numerical models during MOI. These new models have not yet yielded predictions of source-receptor relationships and are still to be validated with monitoring data.



## 2.1 PRESENT DAY ACID FORMING EMISSIONS IN NORTH AMERICA

Knowledge of sources and emissions of pollutants is essential to define the problem of long range transport and for any scientific analysis of the linkages between releases of pollutants to the atmosphere and possible environmental effects hundreds to thousands of kilometres downwind of the emitting sources. The current concern is primarily with the oxides of sulfur and nitrogen both of which give rise to what has become known as acid deposition. It is generally accepted that the acid forming potential of sulfur dioxide ( $\text{SO}_2$ ) emissions in eastern North America is currently twice that of nitrogen oxides ( $\text{NO}_x$ ) emissions.

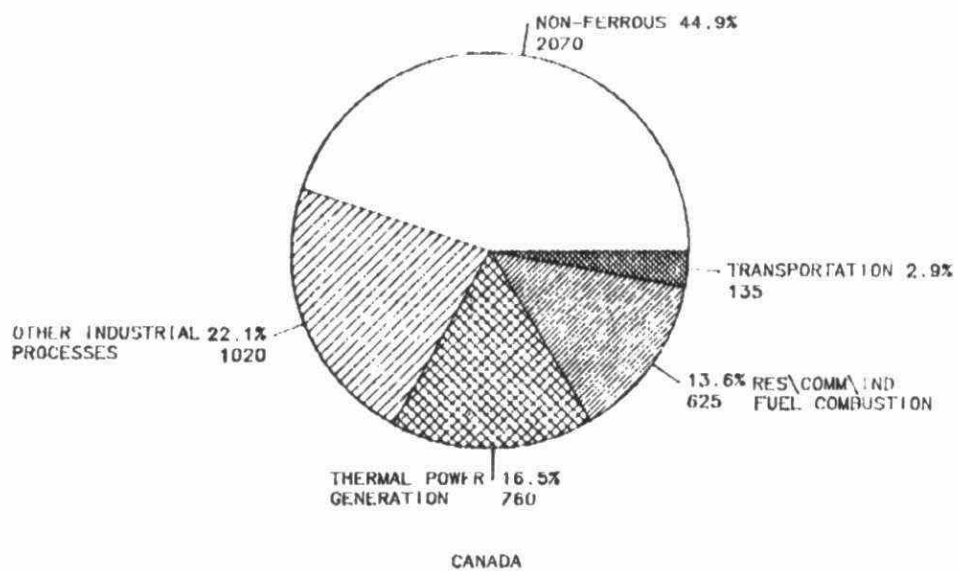
### 2.1.1 Anthropogenic Emissions

The most complete picture of the emissions of  $\text{SO}_2$  and  $\text{NO}_x$  from anthropogenic sources is for the base year 1980, originally presented in MOI (1982a). Improvements to the information presented in the MOI report have been made in Canada and the United States to support second generation long range transport models. In the U.S., efforts to improve the 1980  $\text{SO}_2$  and  $\text{NO}_x$  emission estimates have been done under the National Acid Precipitation Assessment Program (NAPAP), Task Group B, "Man-Made Sources" (EPA, 1984). The current NAPAP inventory also includes emissions of other pollutants important in acid deposition research namely, volatile organic compounds (VOC), ammonia, primary sulfate and particulates. Further refinements including speciation of VOC's and  $\text{NO}_x$  emissions and temporal and spatial resolution of emissions into small grids are nearing completion (Mobley, 1985).

In Canada, similar efforts carried out under the national inventory program (EPS, 1985a) have resulted in improvements to the emission estimates of  $\text{SO}_2$  and  $\text{NO}_x$ . The national inventory also includes estimates of VOC's, primary sulfates and particulates which, together with the emissions of  $\text{SO}_2$  and  $\text{NO}_x$ , have been incorporated into the NAPAP inventory. Specific studies have also been done on the sources and emissions of ammonia (EPS, 1985b) on the emissions of alkaline constituents from man-made sources (MEP, 1984), on speciation of VOC's (EAG, 1985) and on the temporal distribution of emissions (MEP, 1985).

The improvements made to the  $\text{SO}_2$  and  $\text{NO}_x$  emission inventories have not however significantly altered the national emission estimates for the U.S. and Canada originally presented in 1982. The latest estimates of the  $\text{SO}_2$  and  $\text{NO}_x$  emissions for the base year 1980 are shown in Figures 2.1 and 2.2.

# NORTH AMERICAN 1980 EMISSIONS OF SULPHUR DIOXIDE 10<sup>3</sup> Tonnes



10<sup>3</sup> Tonnes

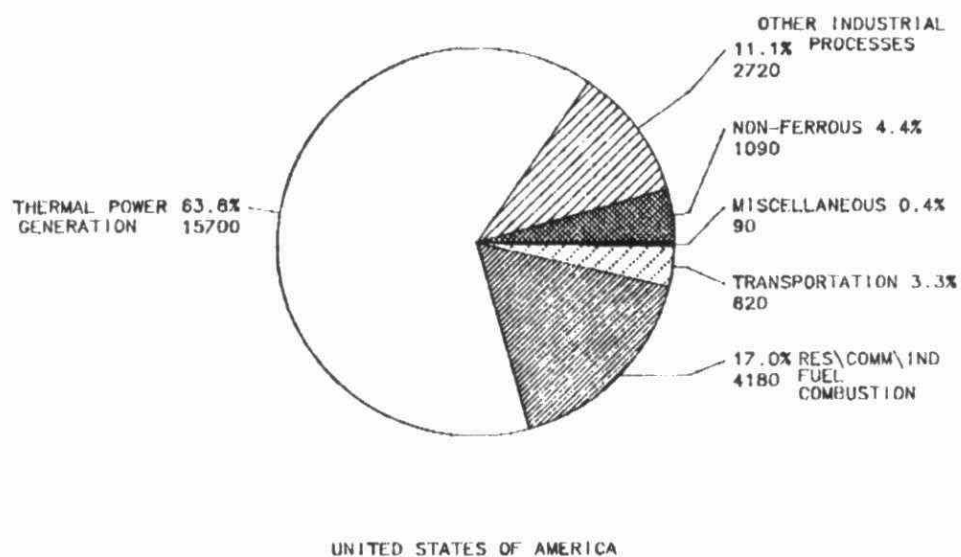
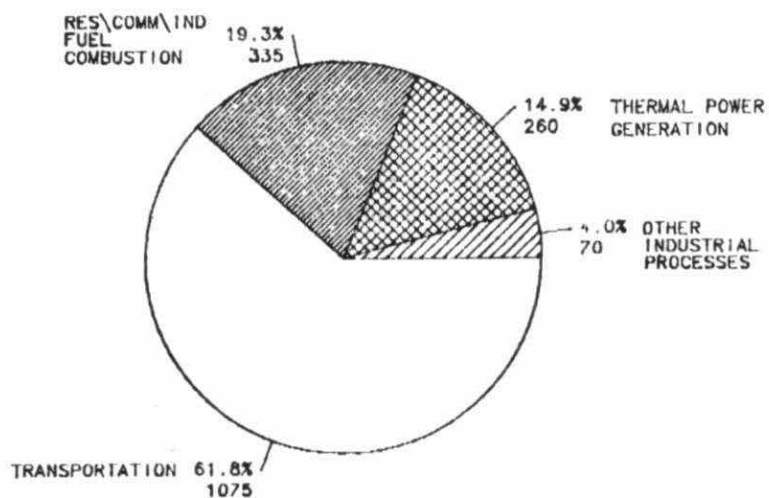
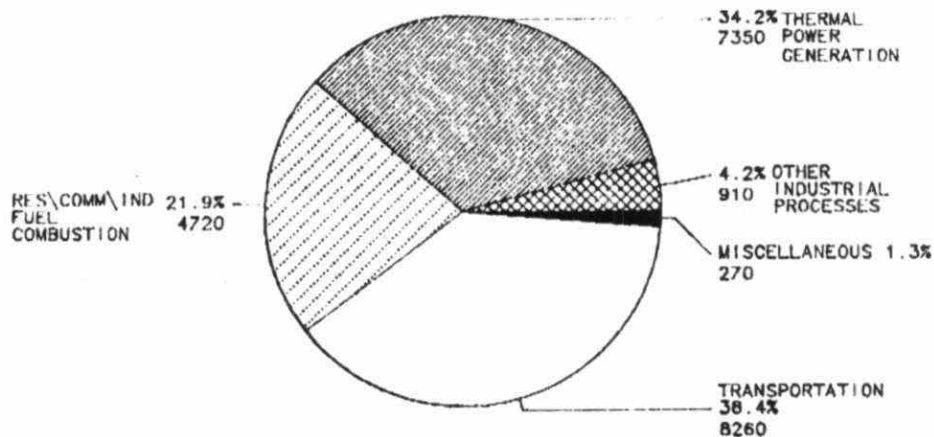


Figure 2.1 Anthropogenic emissions of SO<sub>2</sub> in Canada and the USA in 1980

# NORTH AMERICAN 1980 EMISSIONS OF NITROGEN OXIDES 10<sup>3</sup> Tonnes



CANADA

10<sup>3</sup> Tonnes

UNITED STATES OF AMERICA

Figure 2.2 Anthropogenic emissions of NO<sub>x</sub> in Canada and the USA in 1980

Thermal power generation is the primary source of  $\text{SO}_2$  emissions in the U.S., contributing about two-thirds of the estimated 24.6 million tonnes nationwide. In Canada, the non-ferrous smelting sector dominates, accounting for about 45 percent of the national emission total of 4.6 million tonnes. Regionally, the 31 states east of the Mississippi River and the provinces east of the Manitoba-Saskatchewan border account for more than 80 percent of the emissions in the eastern part of North America where the effects of acid deposition have been most severely felt.

The emissions of  $\text{NO}_x$  (Figure 2.2) are dominated by the combustion of fuels. Transportation and power generation are the most important contributors to emissions, the latter sector being more important in the U.S. than it is in Canada. The emissions of nitrogen oxides are more evenly distributed geographically than is the case for  $\text{SO}_2$ , although the eastern parts of both countries (as defined above) are each responsible for more than 60 percent of the emissions.

A further refinement has been in developing estimates of the seasonal variations of the emissions of  $\text{SO}_2$  and  $\text{NO}_x$ . The data show that, both in the U.S. and Canada, the percentage nationwide emissions of  $\text{SO}_2$  and  $\text{NO}_x$  are roughly equivalent from one season to the next, although the emissions of  $\text{SO}_2$  are somewhat higher in the winter months (EPA, 1984; MEP, 1985). Generally, the variation in emissions from season to season is within 10 percent of the annual average.

Another important component of the  $\text{SO}_2$  and  $\text{NO}_x$  emissions inventories is the estimation of uncertainties associated with the calculation of emission values. The development of methodologies and computer software for dealing with the analysis of uncertainty has continued since the MOI (Benkowitz, 1985). Nevertheless, the analyses presented in MOI (1982a), placing the estimated errors of the  $\text{SO}_2$  and  $\text{NO}_x$  U.S. and Canadian inventories on a national basis at less than 10 percent, are still valid. On a regional basis the errors may be somewhat higher.

#### 2.1.2 Natural Emissions

The estimation of natural emissions of  $\text{SO}_2$  and  $\text{NO}_x$  still have a considerable degree of uncertainty because of the paucity of relevant data. Previous estimates of the emissions of sulfur from natural sources for Canada were in the order of 0.5 million tonnes (EPS, 1980), coming principally from the biogenic activity of soils. The biogenic estimate relied almost entirely on sulfur flux values based on one study completed in 1979 by Adams et al (1981). Recent experiments done at three sites in the eastern United States by the U.S. National Oceanic and Atmospheric Administration (Goldan, et al., 1985) have shown absolute flux values to be about a factor of 10 lower than previously reported. Measurements were based on the use of enclosures that were placed over bare soil, various types of agricultural crops, and naturally occurring vegetative cover. Concurrent measurements of  $\text{H}_2\text{S}$  and total sulfur fluxes by entirely independent techniques substantiate the lower fluxes reported. Although previous estimates of emissions of sulfur from natural sources were low

compared to man-made sources, these new findings would tend to lower the estimates further, reinforcing the fact that natural sources of sulfur emissions do not play a major role in acid deposition at least in eastern North America.

With respect to emissions of  $\text{NO}_x$ , the principle natural sources on the North American continent are lightning and biogenic activity in soils (EPS, 1981; Fehsenfeld et al, 1985). Recent emission estimates also done by the U.S. National Oceanic and Atmospheric Administration (Fehsenfeld et al, 1985), based on the estimates of Logan (1983), updated to account for recent developments reported in the literature, place the emissions of  $\text{NO}_x$  in North America at 0.3 million tonnes (N) from lightning and 0.6 million tonnes (N) from soils, annually. As is the case for  $\text{SO}_2$ , the current state of knowledge would tend to suggest that  $\text{NO}_x$  emissions from natural sources are small compared to anthropogenic emissions.

Work is underway on, and preliminary data are also available for, the emissions of other substances involved in the chemistry of acid rain information (e.g. alkaline materials, photochemically reactive hydrocarbons), but the emission estimates are highly uncertain.

## 2.2 CHANGES IN EMISSIONS OVER THE LAST 30 YEARS\*

Historical emissions of  $\text{SO}_2$  and  $\text{NO}_x$  are presented in Figures 2.3 and 2.4 for the U.S. and Canada respectively. The U.S. data are taken from their latest national emissions trends report (EPA, 1986) and are the most complete and consistent data set available for a retrospective analysis of the overall changes in emissions on a national scale. The emission values for 1980 may differ slightly from those shown in Section 1 developed under the NAPAP program, where the focus was exclusively on the 1980 base year inventory.

Emissions of  $\text{SO}_2$  in the U.S. rose from close to 20 million tonnes in 1950 to about 28 million tonnes in 1970 before dropping to about 24 million tonnes in 1980. In the midwestern states of Illinois, Indiana, Michigan, Minnesota, Ohio and Wisconsin,  $\text{SO}_2$  emission levels in 1980 were about 25 percent higher than in 1955, although they have been on the decline since the mid-1960's (MOI, 1982a).

Nitrogen oxides emissions in the U.S. increased substantially in all areas over the 1950-80 period. This increase ranged from a factor of two in the northeast to over three in the south (MOI, 1982a). The total U.S.  $\text{NO}_x$  emissions have increased steadily from about 9 million tonnes to about 21 million tonnes and did not peak between the mid-1960's and early 1970's as did  $\text{SO}_2$ . In the eastern U.S., emissions which were at a level of about 6 million tonnes in 1950, reached levels of more than 12 million tonnes in 1980.

Changes in the geographical location of sources are not well documented. In the northeast portion of the U.S. there has been some redistribution of  $\text{SO}_2$  emissions from small urban sources to large (power plant) rural sources (EPA, 1985). There has been a major shift in the U.S. population to the southern states and with it a proportional increase in the southern emissions (MOI, 1982a).

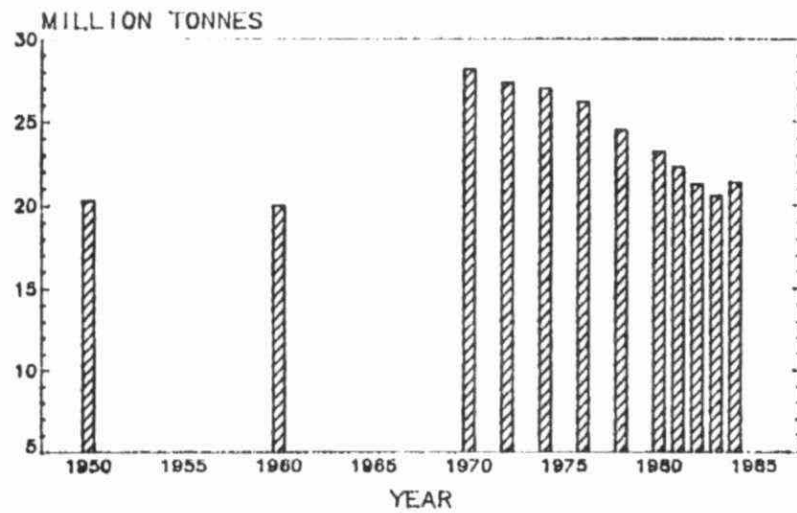
Total Canadian emissions of  $\text{SO}_2$  (Figure 2.4) were approximately 4.6 million tonnes in 1980, about the same level as in 1955, after having peaked between the mid-1960's and 1970 at about 6.7 million tonnes (MOI 1982a, EPS 1985a, EPS 1986). Eastern Canada contributed the bulk of these emissions, i.e. 4.3 million tonnes in 1955, 5.6 million tonnes in 1965 and 3.8 million tonnes in 1980. Total  $\text{NO}_x$  emissions in Canada have increased from 0.6 million tonnes in 1955 to 1.7 million tonnes in 1980. Eastern Canada has contributed more than 60 percent to these emissions over this period.

As shown in Figures 2.3 and 2.4, estimates of the emissions of  $\text{SO}_2$  show a continuing downward trend during the early 1980's. This was due in part

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\*Prepared by F. Vena, D. Yap and E. Voldner

### HISTORICAL EMISSIONS IN THE UNITED STATES SULPHUR DIOXIDE



### HISTORICAL EMISSIONS IN THE UNITED STATES NITROGEN OXIDES

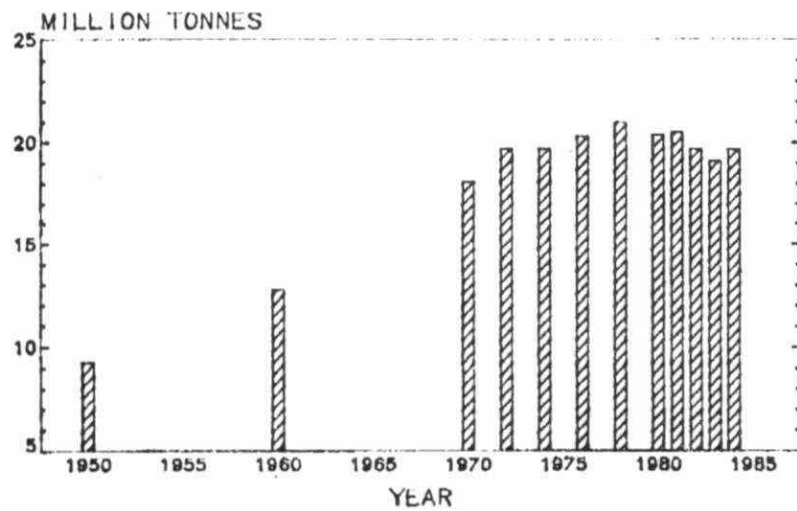
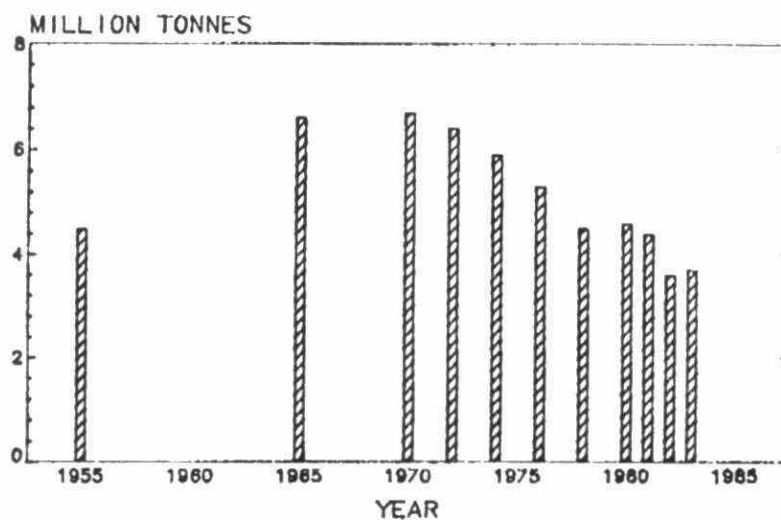


Figure 2.3 Historical anthropogenic emissions of  $\text{SO}_2$  and  $\text{NO}_x$  in the USA

### HISTORICAL EMISSIONS IN CANADA SULPHUR DIOXIDE



### HISTORICAL EMISSIONS IN CANADA NITROGEN OXIDES

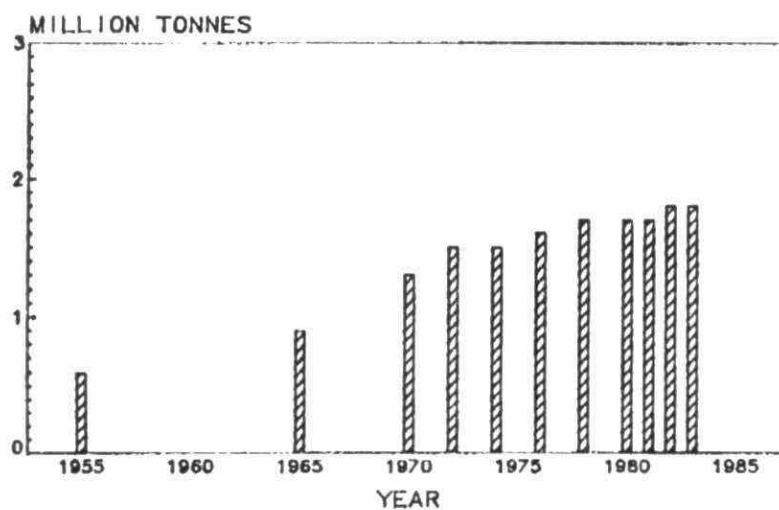


Figure 2.4 Historical anthropogenic emissions of  $\text{SO}_2$  and  $\text{NO}_x$  in Canada



to the economic recession experienced during this period and indications are that SO<sub>2</sub> emissions may have increased again slightly between 1983 and 1985 in response to the economic recovery. Such short term fluctuations from longer term trends given the present state of emission controls are expected to continue in response to the level of economic activity. During the same period emissions of NO<sub>x</sub> in the U.S. have decreased slightly and in Canada have remained relatively constant.

There have been some important changes in the characteristics of the emission sources over the last 30 years. An analysis performed by Gschwandtner (1985) for the U.S. EPA shows historical national emissions of SO<sub>2</sub> and NO<sub>x</sub> by stack height ranges (Figure 2.5). The analysis suggests that more SO<sub>2</sub> emissions were released into the atmosphere from stacks taller than 73 m, than from shorter stacks since about 1945. By 1980, approximately 30 percent of the SO<sub>2</sub> emissions were emitted from stacks above 146 m. Approximately 60 percent of the total NO<sub>x</sub> emissions in 1980 were released from ground level sources; predominantly from transportation sources.

This progressive increase in the proportion of SO<sub>2</sub> and NO<sub>x</sub> from tall stacks has enhanced the potential for long range transport of these emissions.

The implications associated with other changes in emission characteristics are not as evident. For example, particulate control devices which are currently widely used in industry, have tended to reduce the emissions of alkaline particulates which were previously emitted to the atmosphere (Sequeria, 1982; Tanner et al., 1981). This would appear to suggest that there has been some reduction in the emissions of neutralizing constituents emitted to the atmosphere. However, estimates have shown that in Canada, the contribution of industrial and fuel combustion sources to particulate alkaline emissions, in comparison to such open sources as paved and unpaved roads, agricultural tilling, construction activity and wind-blown soil dust, is small, typically less than 2 percent (MEP, 1984). Prior to the introduction of particulate controls on industrial sources, this percentage would have been higher, but given the magnitude of open source emissions, the contribution to total alkaline emissions would still have been relatively small.

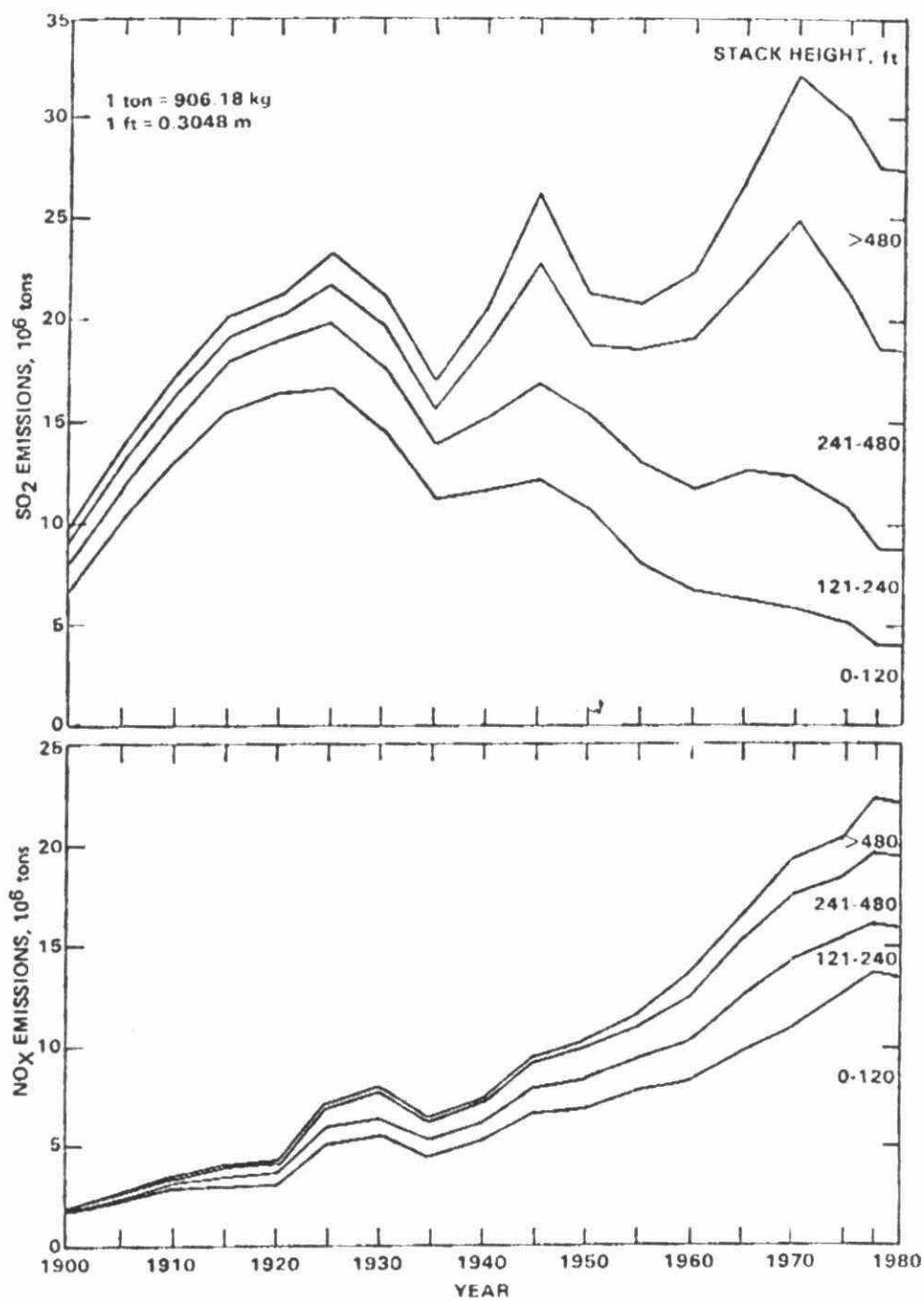


Figure 2.5 Historical total United States national SO<sub>2</sub> and NO<sub>x</sub> emissions by stack height ranges

## 2.3 CURRENT CONCENTRATION AND DEPOSITION PATTERNS

### 2.3.1 Wet Deposition\*

The MOI reports, and most of the publications since then, which discuss the general large-scale aspects of wet deposition, have tended to concentrate on observations for the year 1980. But monitoring has continued, and in many cases expanded, so that there is now increased spatial coverage and a much larger data base to work with. As a result the number of papers presenting results from the analysis and interpretation of wet deposition observations has increased dramatically in the last few years. In this section, some of the more important new findings will be presented starting with a brief discussion of the global picture and then concentrating on the North American situation with emphasis on the east where acid deposition is already a serious large-scale regional issue.

#### 2.3.1.1 Global Deposition and Background pH

The Global Background Air Pollution Monitoring Network (BAPMoN) continues to be operated by the World Meteorological Organization (WMO) and the United Nations Environment Program (UNEP) but, very little in the way of detailed analysis of the observations has been published. A global network of remote sites has been operated by NOAA since the early 1970's and has expanded with time to include some research sites directed by the University of Virginia (Dayan et al., 1985). It is from the latter sites that Galloway et al. (1984) have been able to establish the background concentration of the  $H^+$ ,  $SO_4^-$  and  $NO_3^-$  ions in precipitation in the remote regions of the world as shown in Table 2.2.

Table 2.2 The observed range of the volume-weighted mean concentrations in precipitation in remote sites around the world (source: Galloway et al., 1984)

	$H^+$	$**SO_4^-$ [ $\mu$ eq $l^{-1}$ ]	$NO_3^-$
Remote Concentrations	10-20	3-10	2-5

\*\*corrected for sea-salt contribution

\*Prepared by P.W. Summers

Note that the range of  $H^+$  in Table 2.2 corresponds to pH values of 4.7 to 5.0. This adds further evidence to the theoretical arguments of Charlson and Rodhe (1982) that the global background pH should be closer to 5.0 than the previously assumed 5.6 based on equilibrium of rainwater with atmospheric  $CO_2$ .

### 2.3.1.2 North American Wet Deposition

a) Long-Term Average Deposition Patterns The wet deposition patterns for the one year 1980, based on the work under the MOI, have been summarized and discussed by Barrie and Hales (1985). Maps for the  $SO_4^{2-}$  deposition for each of the years 1981 through 1983 (Summers et al., 1985) show basically the same pattern as for 1980, with some year-to-year variation in the position of specific deposition contours (see Figure 2.6). Both the location and size of the pockets of maximum deposition ( $> 40 \text{ kg ha}^{-1} \text{ y}^{-1}$ ) change considerably from year to year, but always remain in the region of southern Ontario, Ohio, New York, Pennsylvania and West Virginia. These changes are a complex function of the emission source strength, wind fields and precipitation patterns. Sufficient data are now available to investigate the year-to-year changes of all the major ions measured in precipitation and to construct the five-year average patterns.

More extensive sampling is now being carried out in the western half of the United States than in 1980 and several regions with the average pH consistently below 5.0 are beginning to show up (Roth et al., 1985). In western Canada the national network has been supplemented by an increasing number of local networks (both provincially and federally operated). It is still difficult to draw meaningful contours in British Columbia because of the strong topographical effects on wind flow and precipitation patterns, but there is a region in the lower Fraser Valley, Gulf Islands with average pH below 5.0, associated with elevated  $SO_4^{2-}$  and  $NO_3^-$  values, contiguous with a similar region in northern Washington State.

The Southern Coastal Network of 13 stations operated in B.C. with locations around the southern end of Vancouver Island, across the Gulf Islands to Vancouver, and 100km up the Fraser Valley has been operated since 1983. Averaged over all precipitation events with a westerly flow in 1983 the pH varied between 5.3 and 5.8. With southerly flows the range of average pH was 4.8 to 6.0 with the lowest values in the Gulf Islands.

In the Prairie Provinces average rainfall pH is well above 5.6 in the south, but through the north, and extending into the Yukon and the NWT pH values vary between 5.0 and 6.0. In these regions, there is no correlation between pH and  $SO_4^{2-}$  concentration because of the confounding effects of the  $SO_4^{2-}$  derived from the soil components found in the rain. The role of alkaline materials in precipitation chemistry of the mid North American continent is now better established although still somewhat controversial. The issues have been reviewed by Gatz et al., 1985 who claim that in the 31 "eastern" States alkaline emissions from open sources for



Figure 2.6 Annual sulfate deposition ( $\text{Kg ha}^{-1}\text{yr}^{-1}$ ) in eastern North America for the years 1981, 1982 and 1983.

[Source: Summers et al., 1985]

particles less than  $10\ \mu\text{m}$  come from wind erosion, tilling and unpaved roads, with the latter accounting for 72% of the total. The effects of unpaved roads are discussed in more detail by Barnard et al., 1985. Only limited analysis has been carried out to assess the magnitude of such sources in Canada.

Because of the small amount of precipitation in the Canadian arctic, and the difficulties in collecting snow in winter, little information is available on the precipitation chemistry. Limited observations suggest wet  $\text{SO}_4^{2-}$  deposition rates  $< 3.0\ \text{kg ha}^{-1}\ \text{y}^{-1}$  and pH values  $> 5.0$ , i.e. values close to the "global background" reported by Galloway et al., (1984).

b) Annual Cycle As the period of record increases in length, the shorter time period variations are being documented more quantitatively and with more confidence. Two important aspects are now well established - the annual cycle and the episodic nature of wet deposition. There is still some difficulty in establishing long term trends with any confidence (see section 2.4.1).

The annual cycle can be demonstrated in several ways. First, by grouping stations together in small regions that have similar characteristics such as climate, topography, land-use and relationship to pollutant source regions, monthly average values of precipitation chemistry concentration/deposition over several years can be determined (Barrie and Sirois, 1982). Such an analysis was presented for four sensitive receptor regions in eastern North America by Summers et al., (1985) and the results for the two Canadian regions are shown in Figures 2.7 and 2.8. The strong annual cycle in most of the major ions shows up clearly, but not necessarily in phase. For example,  $\text{H}^+$  and  $\text{SO}_4^{2-}$  are highly correlated and have a well-marked summer maximum. The impact of the stormy winter season shows up in the sea-salt chloride deposition in the Maritimes.

A second way to present these data (Bowersox and Stensland, 1985) in a simplified form is by means of the ratio of the concentration during the warm biologically active period (May through September) to the cold dormant period (November through March). Examples for  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations are shown in Figure 2.9. The warm/cold season ratios of deposition (Summers et al., 1985) for several species are shown in Table 2.3. The acidic components  $\text{H}^+$  and  $\text{SO}_4^{2-}$  clearly maximize in the warm season over eastern North America. In Canada the warm and cold period deposition of  $\text{NO}_3^-$  are equal.

**CENTRAL ONTARIO / SW QUEBEC ( 1980-1983 )**  
**WET DEPOSITION (kg ha<sup>-1</sup> month<sup>-1</sup>)**

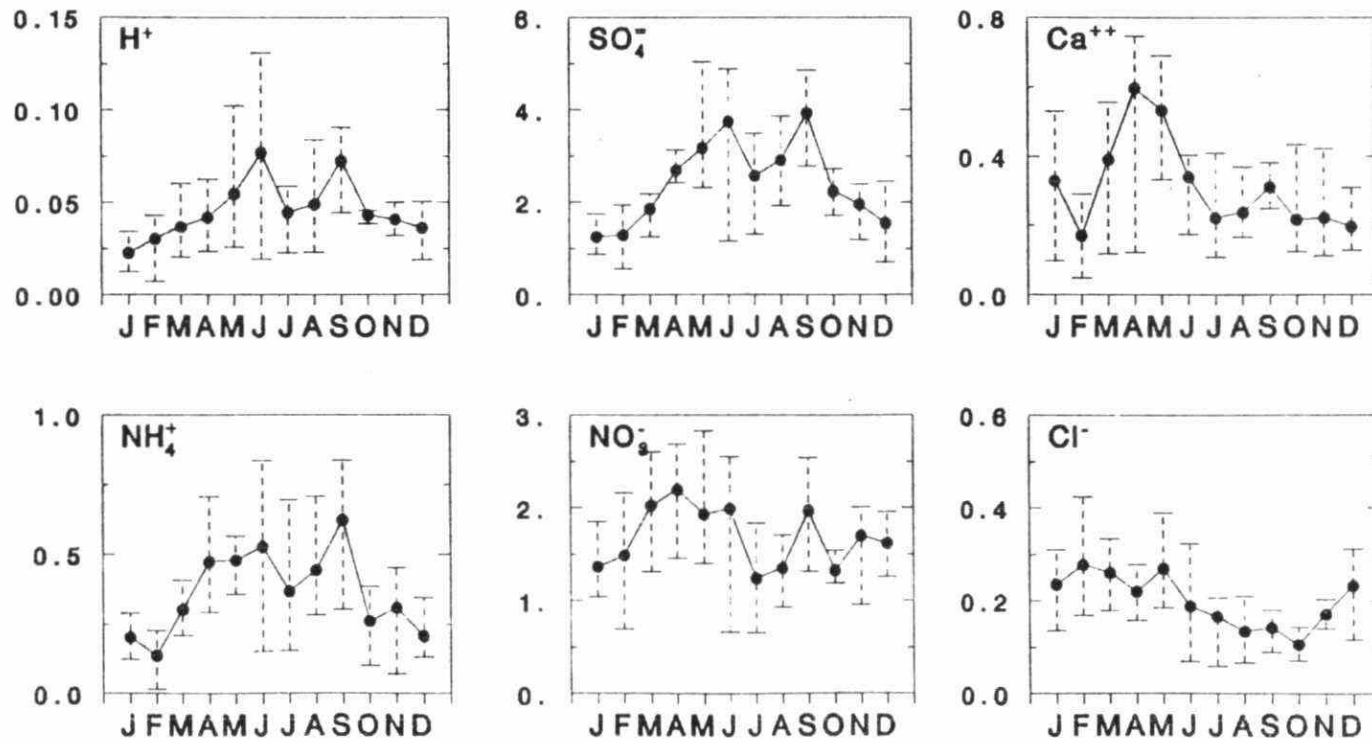
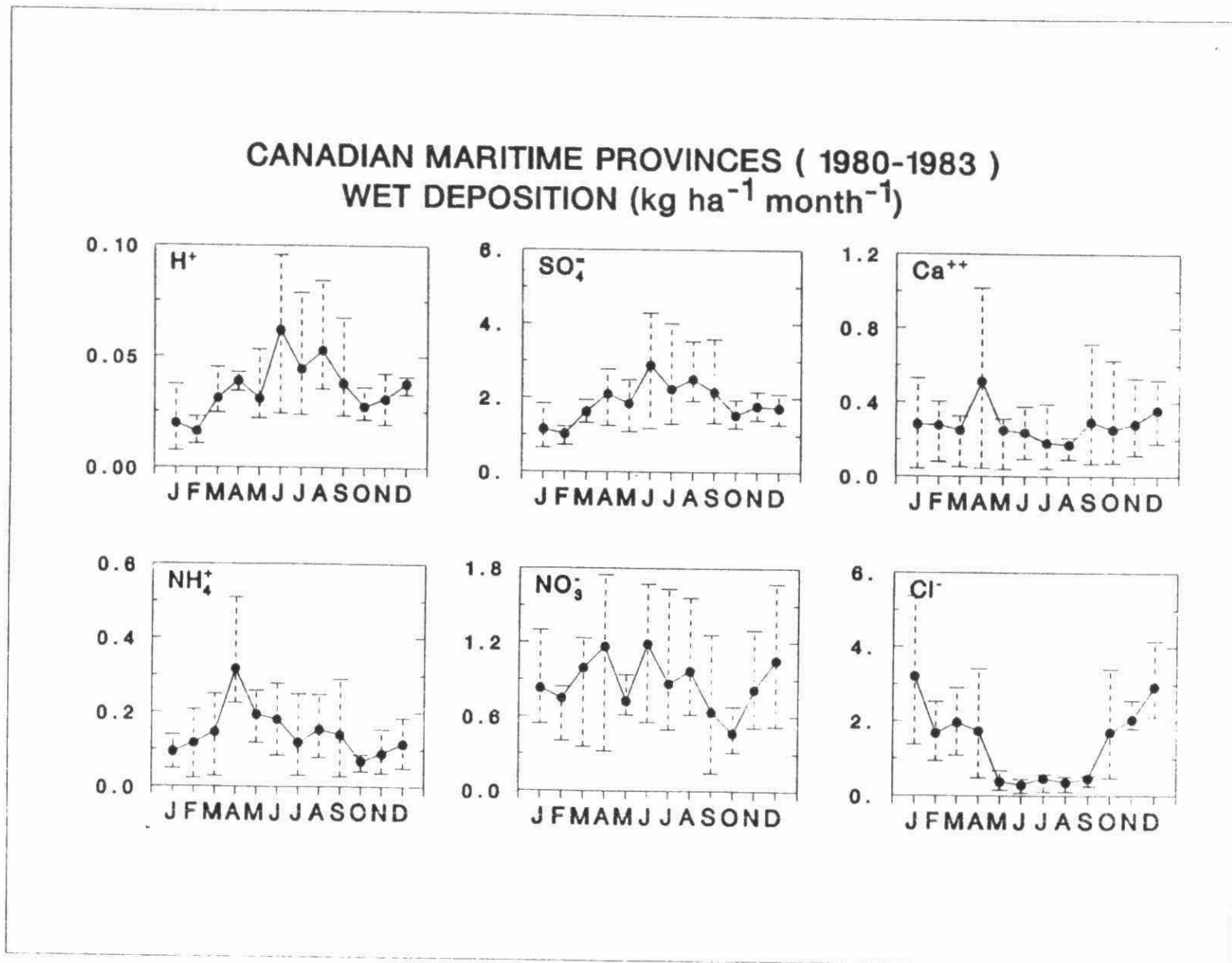


Figure 2.7 The annual cycle of the major ions in precipitation across the Canadian Shield area of central Ontario and SW Québec

Figure 2.8 The annual cycle of the major ions in precipitation in the Canadian Maritime Provinces





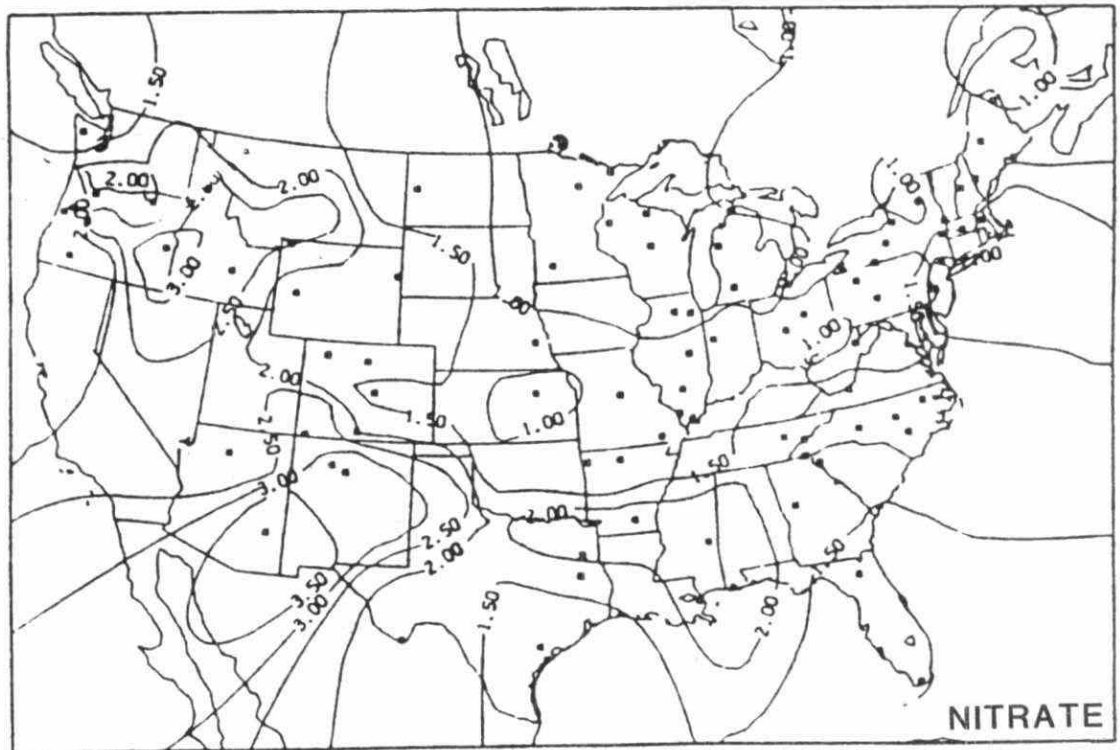
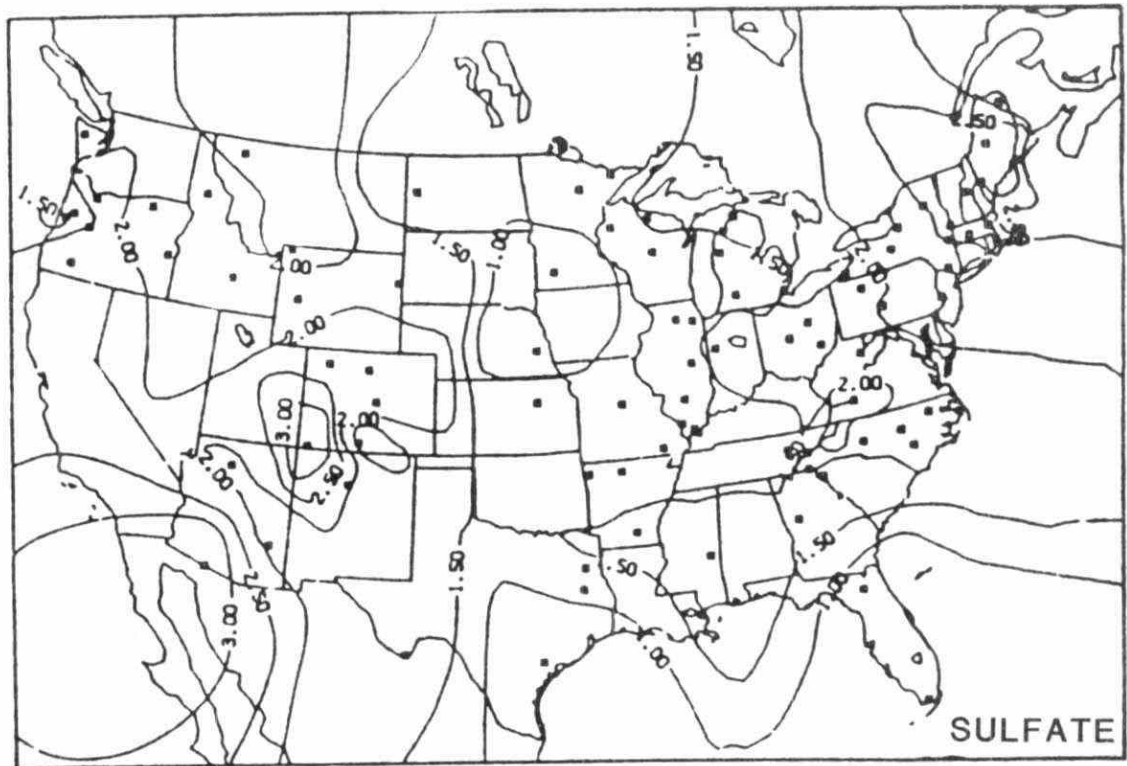
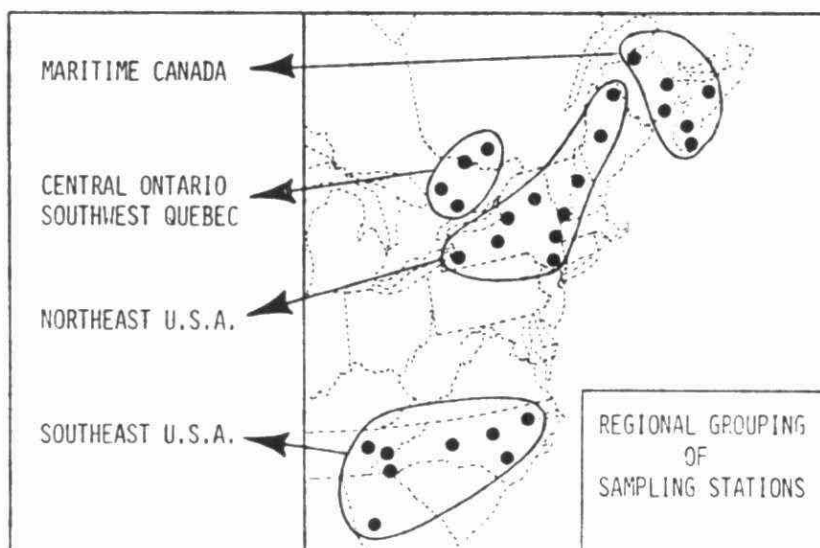


Figure 2.9 The ratio of the warm period (May - Sept) to the cold period (Nov - Mar) median concentrations in precipitation: a) for sulfates, b) for nitrates.

[Source: Bowersox and Stensland, 1985]

Table 2.3 Intra-annual variability of the wet deposition of the major ions expressed as the mean and coefficient of variation for the warm to cold season ratio for the four groupings of stations indicated on the map below.

	Ratio of Warm/Cold Season Deposition				Coefficient of Variation
	Southeast USA	Northeast USA	Central Canada	Maritime Canada	
H <sup>+</sup>	1.80	2.32	1.78	1.67	18-25%
SO <sub>4</sub> <sup>=</sup>	1.63	2.60	2.05	1.59	
NO <sub>3</sub> <sup>-</sup>	1.58	1.54	1.04	0.99	
NH <sub>4</sub> <sup>+</sup>	1.86	2.94	2.09	1.40	
Ca <sup>++</sup>	1.30	1.83	1.25	0.78	35-45%
Mg <sup>++</sup>	0.98	1.48	1.46	0.27	
K <sup>+</sup>	1.34	2.22	1.07	0.42	
Na <sup>+</sup>	0.74	0.90	0.60	0.18	
Cl <sup>-1</sup>	0.62	0.94	0.78	0.17	50-70%



c) Episodicity The Episodic nature of wet deposition events is now well-established from the analysis of data from various networks. Daily events of heavy rates of wet deposition are infrequent, but in eastern North America account for a large fraction of the annual total deposition. When the daily values are ranked in order of  $H^+$ ,  $SO_4^{2-}$  or  $NO_3^-$  deposition, it is found that over a long period (a year or more) the top 20% of these events account for 50% or more of the total deposition during the period (Whelpdale and Barrie, 1982). Barrie and Sirois (1985) have defined "episodicity", as the fraction (%) of the total dry or wet deposition in a period that occurs in the 20% highest ranked deposition events. The episodicity of the deposition at the Canadian APN sites is shown in Table 2.4.

Consecutive days of heavy deposition are rare events and only occur when the right combination of meteorological factors persist for several days. An exceptional case of such a prolonged episode occurred in southern Ontario during the period 28 August to 4 September 1981 (Kurtz et al., 1984). A nearly stationary low pressure system persisted over the Great Lakes for more than a week and continuously pumped warm, moist, polluted air into southern Ontario from the south. As a result, during this period, Dorset received 100mm of rain (12% of the 1981 total) and a wet deposition of  $7 \text{ kg } SO_4^{2-} \text{ ha}^{-1}$  (28% of the 1981 total).

d) Spatial Variations Within the apparently smooth wet deposition patterns generated by the national networks there is considerable small-scale variability. This is well-illustrated by the regional (Provincial and State) networks now in operation. Three examples are given in Figures 2.10, 2.11 and 2.12, showing respectively the variation in annual  $SO_4^{2-}$  deposition across Ontario, the annual  $SO_4^{2-}$  deposition across Québec and the variation of average pH in Alberta.

The important point is that, for specific locations, interpolation between the sparsely located stations of national networks needs to be done with care.

e) Ionic Interrelationships This is an area of increasing interest because the investigation of the concurrent behaviour of several species is useful for understanding atmospheric processes and is especially important when assessing the ecological response to deposition.

Cluster analysis of wet deposition data in the eastern United States (Gorham et al., 1984) shows clear linkages between species associated respectively with (i) anthropogenic air pollution, (ii) agricultural sources and (iii) sea-spray sources. Gorham showed that the  $SO_4^{2-}$  in precipitation is more closely related than  $NO_3^-$  to the  $H^+$  deposition (or pH) and thus as far as aquatic ecosystems are concerned is the more important anion. However, for other ecosystems, such as forests, nitrate deposition is now considered to be very important.

The whole question of the relative importance of nitrogen species versus sulfur species is now being more thoroughly addressed. Early indications

Table 2.4 The episodicity of dry and wet deposition of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  as indicated by the fraction of total dry or wet deposition in a period (%) that occurs in the top 20% of deposition events.

STATION	DRY		WET	
	$\text{SO}_4^{2-}$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{NO}_3^-$
Long Point	51	51	52	47
Algoma	60	68	70	55
Chalk River	51	62	55	46
Montmorency	61	64	63	58
Kejimikujik	51	56	57	59
ELA	49	62	63	58

(Source: Barrie & Sirois, 1985)

of the higher relative abundance of  $\text{NO}_3^-$  in winter precipitation came from snow sampling in the Adirondaks and in the eastern Canadian Shield (Barrie and Vet, 1984). The ratios of  $\text{SO}_4^{2-}/\text{NO}_3^-$  over a wider region of eastern North America for the year 1980 in relation to the ratio of  $\text{SO}_x/\text{NO}_x$  in emissions was discussed by the National Academy of Sciences (NAS, 1983). This analysis was expanded by Summers and Barrie (1985) to include several years of data and emphasize both the spatial and temporal variations. The most significant findings of the analysis are:

- i) the strong seasonal variation in the molar ratio of  $\text{SO}_4^{2-}/\text{NO}_3^-$  in the region of highest deposition in northeastern North America ranging from about 0.5 in winter to 1.3-1.5 in summer (see Figures 2.13 and 2.14). Note the large region over the Great Lakes and New England (see Figure 2.14) where nitrate contributes almost as much as sulfate to the December to February precipitation acidity and hence to the accumulating snowpack.
  - ii) the reversal of the phase of the annual cycle in the Texas/Louisiana region compared to the NE (see Figure 2.15) even though in both regions there is no significant annual cycle in the ratio of  $\text{SO}_x/\text{NO}_x$  emissions.
- e) Wet Deposition via Fog and Low Cloud Another aspect of wet deposition that has come to the fore in recent years is that due to low clouds and fog. This is important because many of the forested areas of eastern North America are on elevated terrain and are thus frequently in contact with low clouds (mountain fogs). For example, the higher elevation forests in

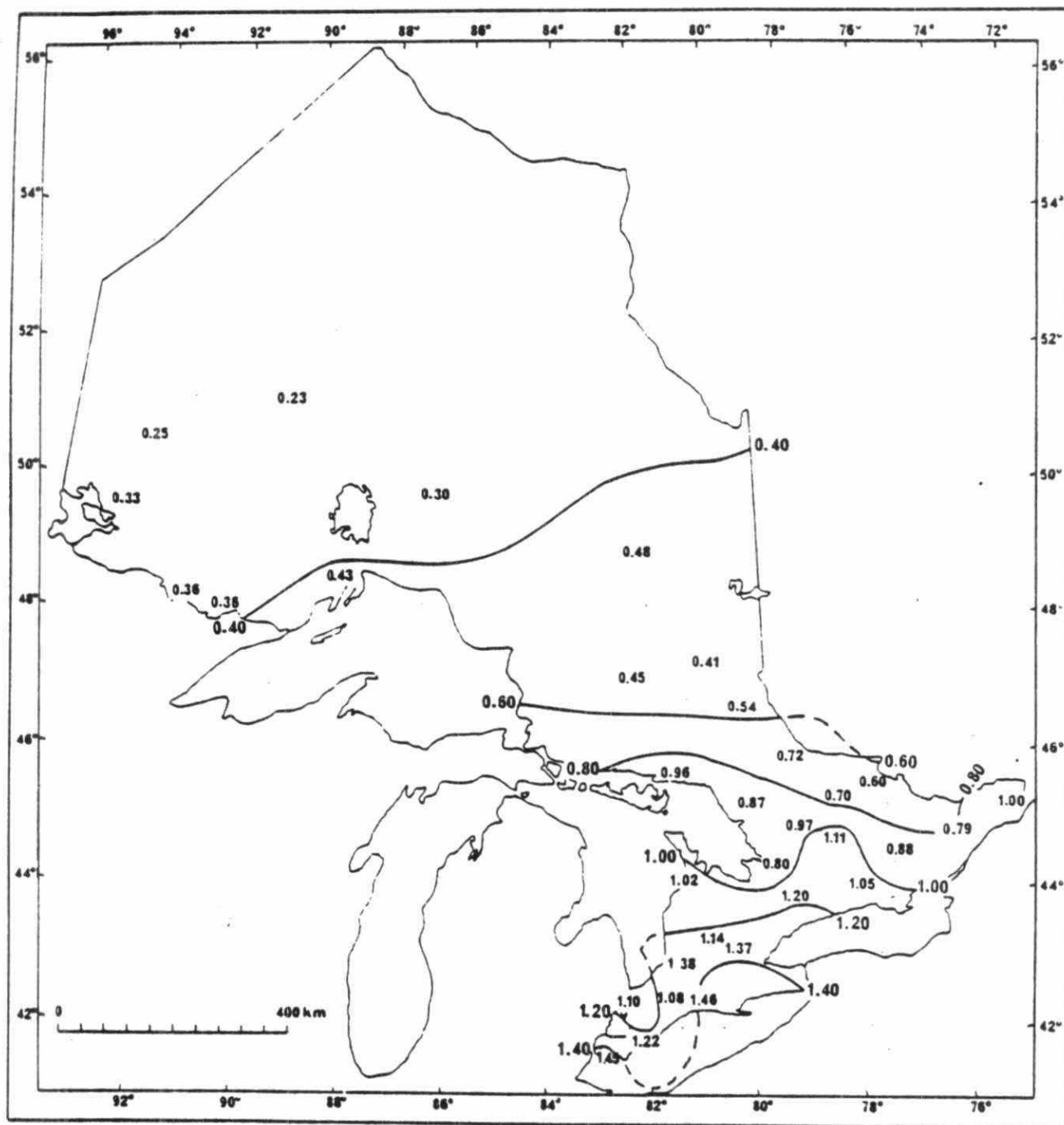


Figure 2.10 The annual wet deposition of sulfate ( $\text{g S m}^{-2} \text{yr}^{-1}$ ) in Ontario in 1982.

[Source: Chan et al., 1985]

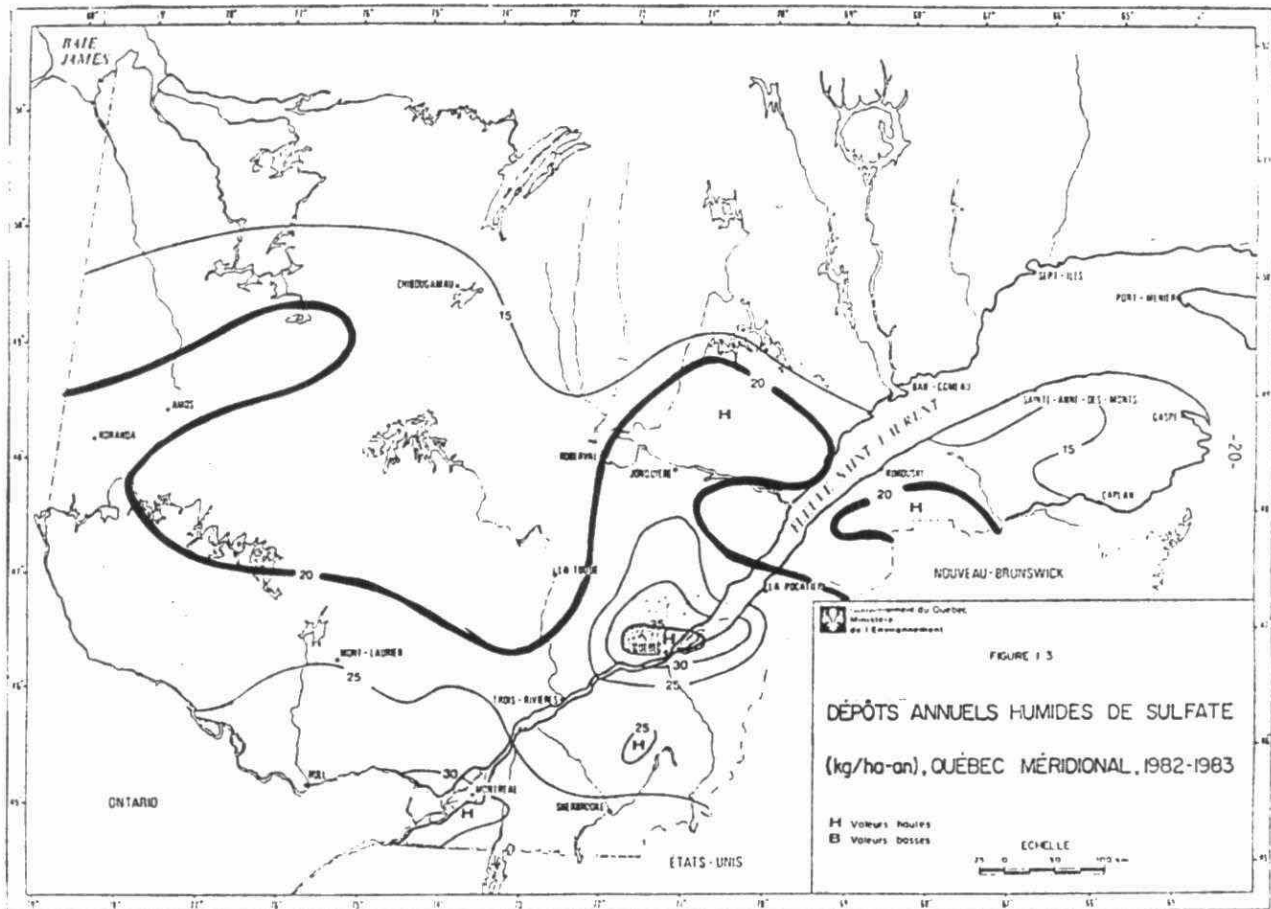


Figure 2.11 Annual average of sulfate deposition in Québec for the two years 1982-1983. [ $\text{Kg SO}_4 \text{ ha}^{-1} \text{ yr}^{-1}$ ]

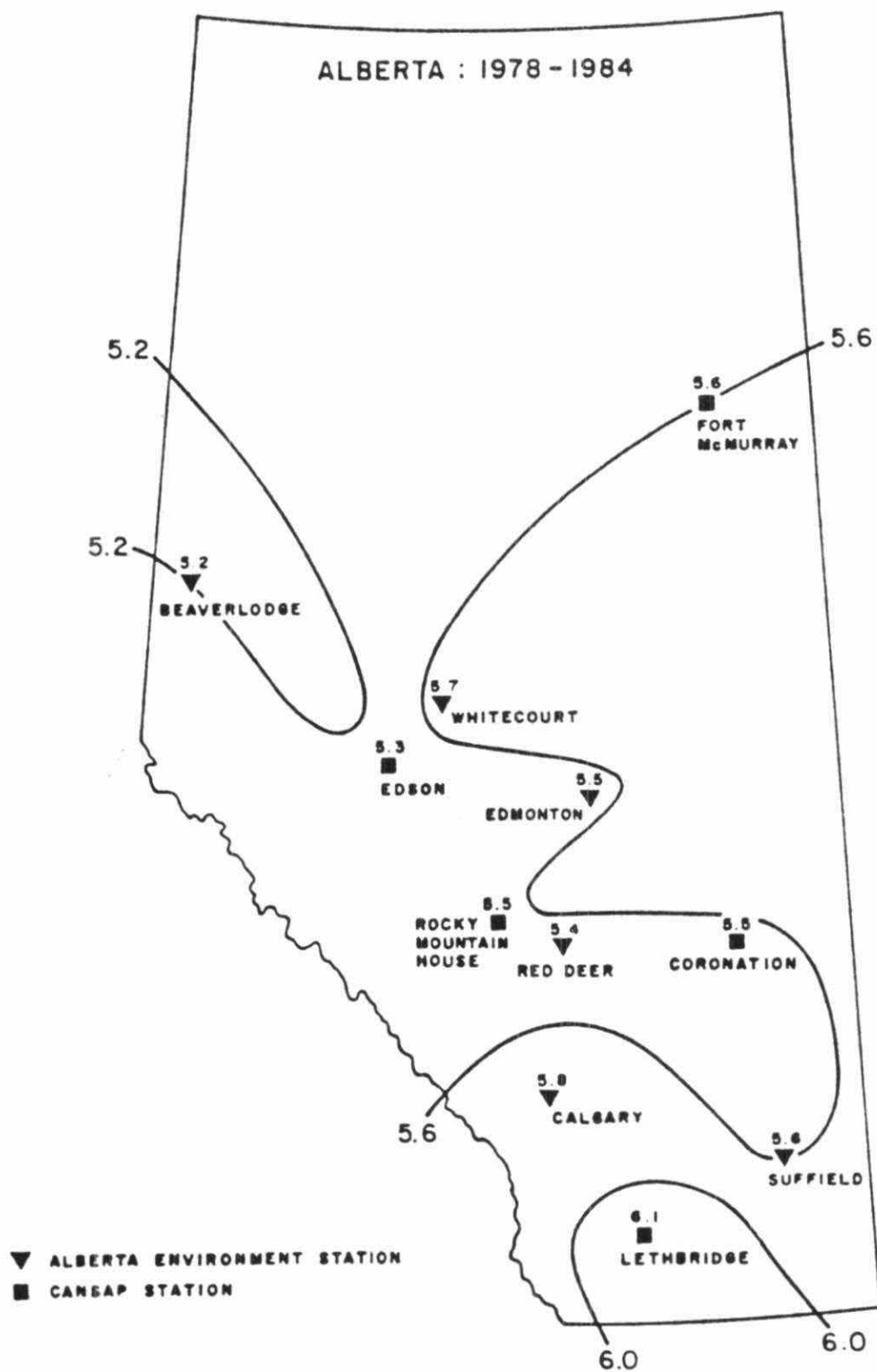


Figure 2.12 The average pH of precipitation in Alberta for the period 1978-1984.

[Source: Lan and Das, 1985]

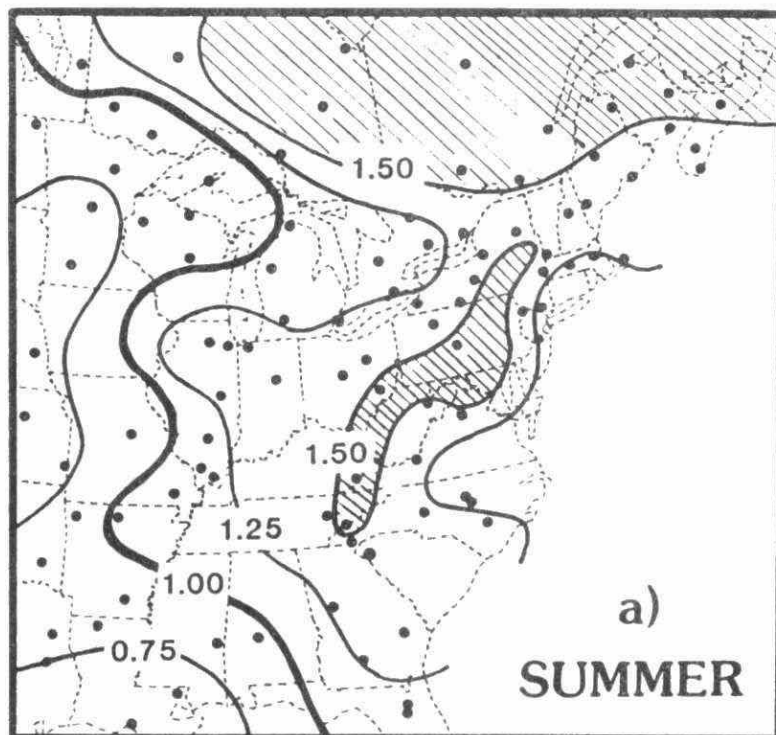


Figure 2.13 The average summer season (June to Aug) value of the  $\text{SO}_4^{2-}/\text{NO}_3^-$  molar ratio in precipitation 1980-1983  
[Source: Summers & Barrie, 1985]

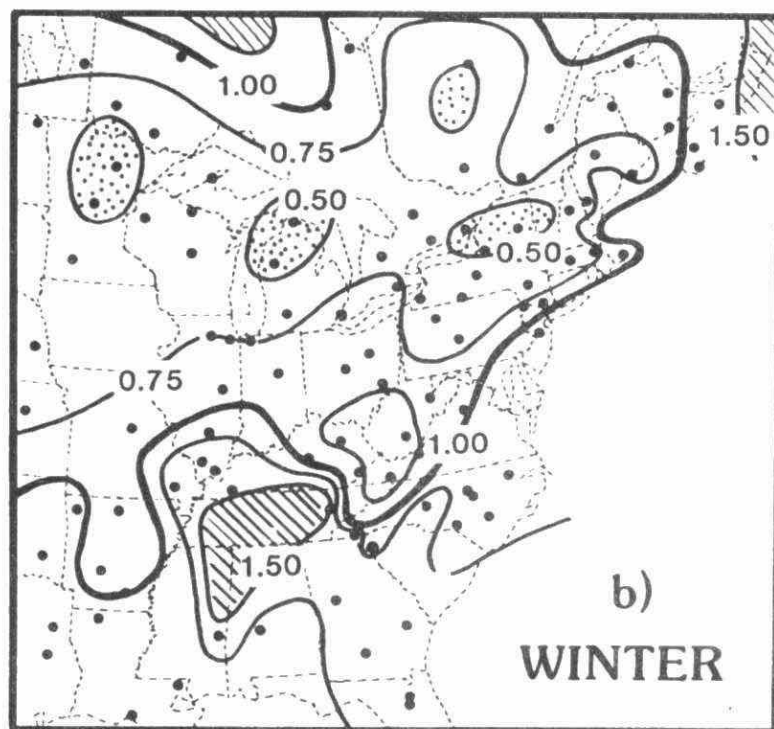
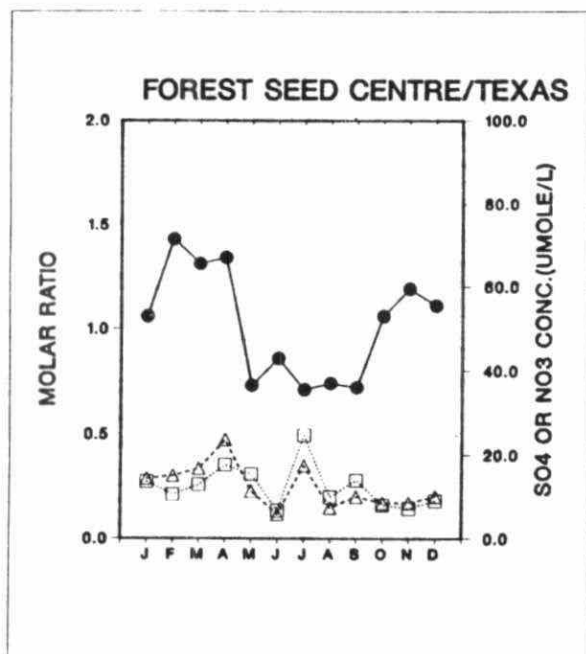
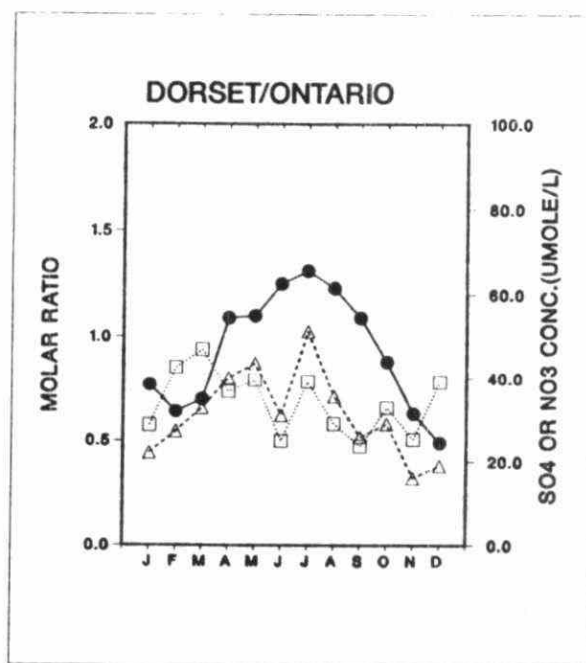
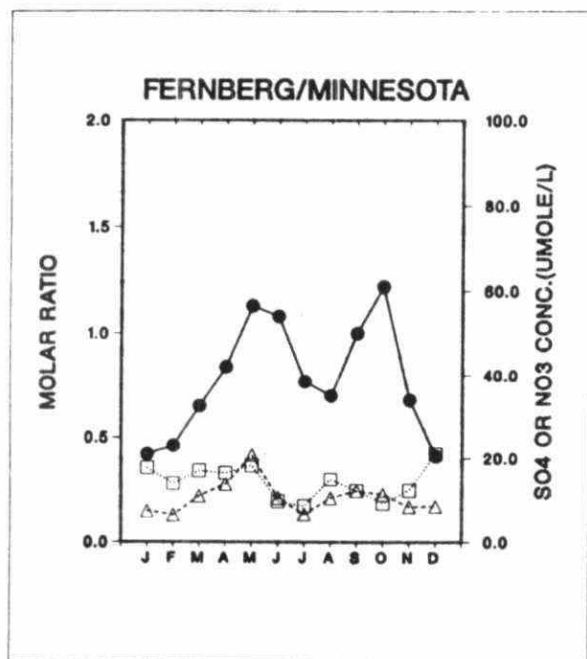


Figure 2.14 The average winter season (Dec to Feb) value of  $\text{SO}_4^{2-}/\text{NO}_3^-$  molar ratio in precipitation 1980-1983  
[Source: Summers & Barrie, 1985]





#### LEGEND

- $\text{SO}_4^{2-}/\text{NO}_3^-$  MOLAR RATIO
- △  $\text{SO}_4^{2-}$  CONCENTRATION
- $\text{NO}_3^-$  CONCENTRATION

Figure 2.15 The annual cycle of the  $\text{SO}_4^{2-}/\text{NO}_3^-$  molar ratio in precipitation 1980-1983 at three sites in North America  
[Source: Summers & Barrie, 1985]

the Green Mountains of Vermont are bathed in cloud water about 10 to 20% of the time (Siccama, 1974). The trees act as efficient collectors of moisture input to the forest. A model to simulate this collection by a balsam fir canopy has been developed by Lovett (1984) and indicates water deposition rates on the order of tenths of a millimeter per hour. The chemical aspects of the deposition mechanisms are described by Barrie and Schemenauer (1985).

Measurements made by aircraft show a strong tendency for the lowest pH to occur near cloud-base, with typical values in the range pH 3.0 to 5.0 (Summers, 1985). The associated concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  range from 10-50  $\text{mg l}^{-1}$  in polluted air masses. Extreme values of 60  $\text{mg l}^{-1}$  have been found in southern Ontario in summer convective clouds (Leaith et al., 1982). Measurements in stratus clouds over the east coast of the United States (Long Island, NY and South Carolina) showed cloud water pH in the range 3.1 to 4.4, with 20% of the  $\text{SO}_4^{2-}$  concentrations exceeding 10  $\text{mg l}^{-1}$  (Daum et al., 1982).

The most extensive series of mountain fog/low cloud measurements have been made atop Whiteface Mountain, New York, at an elevation of 1480 m. Early measurements of pH values in non-precipitating clouds ranged from 3.0 to 4.5, with occasional values below 3.0 (Falconer and Falconer, 1980; Castillo et al., 1983). More recent measurements, reported by Castillo et al., (1985), showed that in the summers of 1981 and 1982 the mean pH of cloud water was 3.5 and 3.9 respectively. In August with polluted southwesterly air flow the mean pH was 2.6 and 3.0 in 1981 and 1982 respectively, with the mean sulfate ion concentrations for these two months being 32  $\text{mg l}^{-1}$ .

When the water flux via cloud droplet impaction is multiplied by the concentrations of  $\text{H}^+$  and  $\text{SO}_4^{2-}$  in the water, the deposition rate can become significant and in some cases exceed that from either precipitation or dry deposition. Deposition by this mechanism is highly dependent on elevation, and the areal extent of eastern North America affected has yet to be determined.

### 2.3.2 Air Concentration and Dry Deposition Patterns\*

The spatial pattern of the concentration of acidic substances in air is an important indicator of the occurrence of air pollution. It is also used to obtain the spatial distribution of dry deposition. In North America, Canada has been a leader in the measurement of air concentrations at rural regionally representative sites. Both the national APN network (Barrie et al., 1984) and the Ontario provincial network, APIOS, (Chan et al., 1985) have been making measurements on a daily or monthly average basis since 1979 and 1981, respectively. As of late 1985, there were no comparable networks in the United States, but these are now being established.

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\*Prepared by L.A. Barrie, E. Voldner and G. den Hartog

Measurements in Ontario are conducted at a sufficient number of sites to yield a good estimate of the spatial distribution of  $\text{SO}_4^=$  and  $\text{SO}_2$  concentrations in air (Figures 2.16 and 2.17). The results show that concentrations are highest in southwestern Ontario near the Detroit-Windsor area and decrease rapidly towards the north and slowly towards the northeast in the direction of the mean wind flow.  $\text{SO}_2$  decreases much more rapidly than particulate  $\text{SO}_4^=$ . This is to be expected since the former oxidizes to produce the latter.

Although air measurements by the federal APN network in eastern Canada are done at fewer sites than in Ontario a good indication of the spatial pattern can be obtained since most sites are far enough from sources that spatial gradients are low. Consequently, fewer sites are needed to obtain a good estimate of the spatial resolution in concentration. The arithmetic mean concentrations of  $\text{SO}_4^=$  and  $\text{SO}_2$  at APN/CAPMoN sites for the period 1979-1984 are shown in Table 2.5. Note the profile of both concentrations across the region with low values in the western and eastern extremes. The highest values are in southern Ontario closest to, and downwind, of the major  $\text{SO}_2$  source regions.

Current direct measurement techniques are not suitable for measuring dry deposition rates routinely (Hicks, 1985). Not only are they difficult and

Table 2.5 Arithmetic mean air concentration measurements at the APN/CAPMoN sampling Sites in  $\mu\text{g-s m}^{-3}$

Site	$\text{SO}_2$	$\text{SO}_4^=$
Cree Lake	0.61	0.32
ELA - Kenora	0.71	0.49
Algoma	1.66	0.91
Longwoods	5.02	1.89
Chalk River	3.61	0.90
Montmorency	1.05	0.59
Kejimkujic	0.84	0.84
Baie d'Espoir	0.32	0.43

costly, but they also require steady meteorological conditions. Thus dry deposition estimates are based on the following approach. It is calculated as the product of a measured or model-predicted air concentration and an areally representative dry deposition velocity. The latter is determined using dry deposition velocities for various surfaces measured in the intensive research studies and a knowledge of the fractional coverage of the area of interest by different surface types (Voldner et al., 1985a).



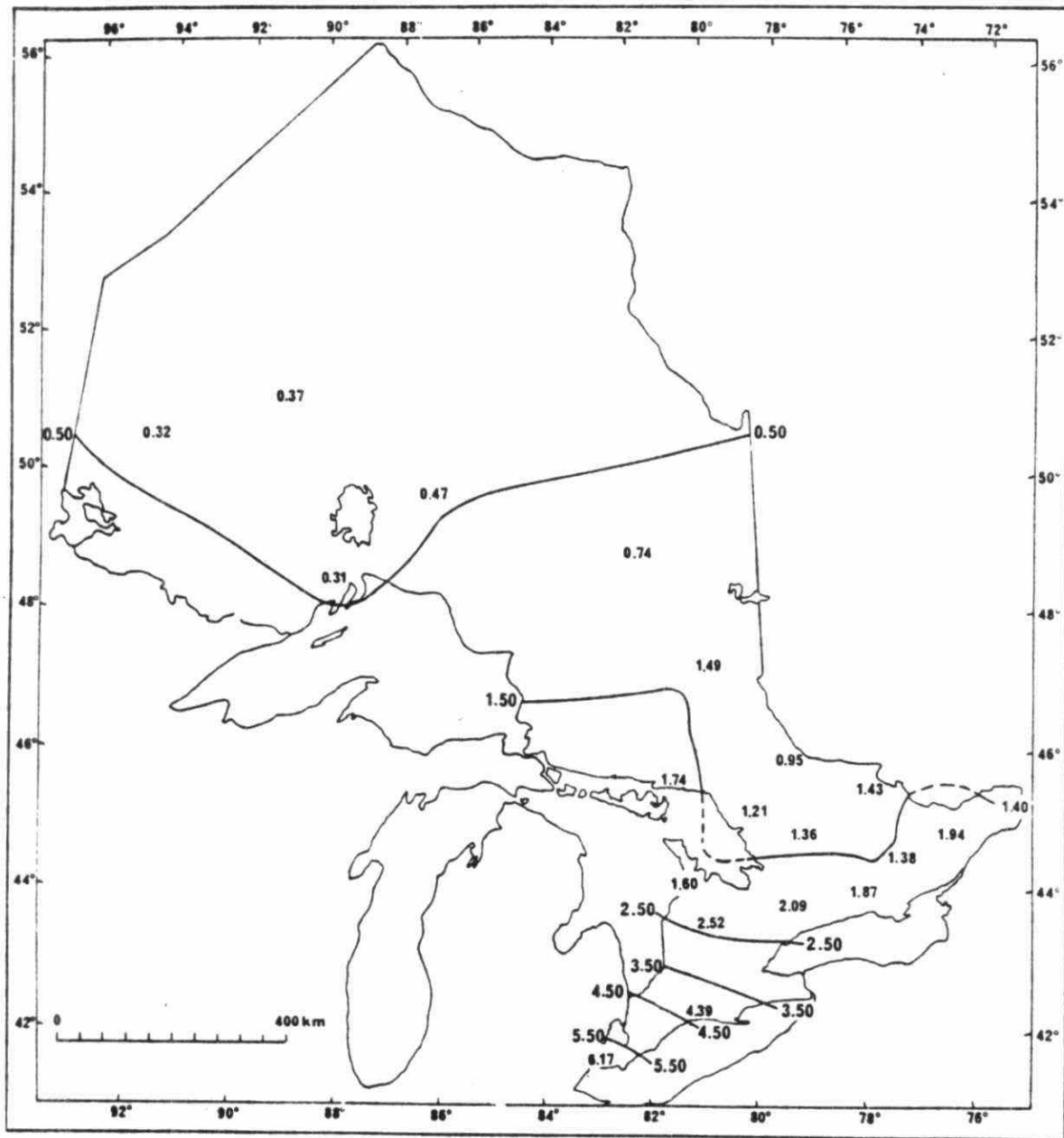


Figure 2.17 The average air concentration of sulfur dioxide ( $\mu\text{g S m}^{-3}$ ) in Ontario in 1982.

Dry deposition fields of sulfur and nitrate for 1982 were estimated by Chan et al., (1985). Air concentrations of  $\text{SO}_2$ , sulfate and nitrate from the APIOS network and dry deposition velocities (Voldner and Sirois, 1986) were used. To estimate dry deposition of nitrate, it was assumed that all nitrate was in the form of nitric acid, which will tend to over-estimate the actual deposition. No measurements of  $\text{NO}_x$  were made. There is clearly a need for instrumental development in this regard.

The results as shown in Figures 2.18 and 2.19 indicate that the annual dry deposition of sulfur, and nitrogen from nitrate, have a south-north, west-east gradient, with the highest values in southwestern Ontario, close to major source regions. The dry deposition fields of  $\text{N-NO}_3$  are more homogeneous than those of sulfur. Thus  $\text{N-NO}_3$  values of about  $0.3 \text{ g N m}^{-2}\text{y}^{-1}$  are observed in southern and south central Ontario. For sulfur, annual deposition of up to  $0.4 \text{ g S m}^{-2}\text{y}^{-1}$  is found in south western Ontario, about  $0.1 \text{ g m}^{-2}\text{y}^{-1}$  in central and  $0.2 \text{ g m}^{-2}\text{y}^{-1}$  in northern Ontario. Most of the sulfur deposition is attributed to deposition of  $\text{SO}_2$ . The results indicate that dry deposition rate of  $\text{SO}_2$  is higher during winter than summer, while  $\text{NO}_3$  deposition is roughly the same throughout the year.

Although not directly comparable, due to the variation in (i) applied dry deposition velocities (ii) assumption of distribution of  $\text{NO}_3^-$  between nitrate particles and  $\text{HNO}_3$ , and (iii) different basis in measurements: results from the APN network (Barrie and Sirois, 1985) confirm the trends observed in the APIOS network, i.e. deposition of  $\text{N-NO}_3$  is more homogeneously distributed than sulfur and the deposition of both sulfur and nitrogen is higher close to emission regions than in remote areas. These patterns are confirmed by model estimates of deposition (Shannon and Lesht, 1985).

Air concentration observations together with deposition velocities can also be used to assess the episodic nature of dry deposition. In eastern Canada 40-70% of the annual sulfur and nitrogen that is dry deposited is delivered during 20% of the days (Barrie and Sirois, 1985).

### 2.3.3 The Relative Importance of Wet and Dry Deposition\*

Ecosystems respond to both wet and dry deposition. In the last LRTAP review done for the MOI, little information on dry deposition was available. However, in the last 5 years a considerable body of information has begun to accumulate that shows a clearer picture of the relative importance of wet and dry deposition of acidic substances in North America. Using information available before 1980, Galloway and Whelpdale (1980) calculated the sulfur budget of the atmosphere over eastern North America. They estimated that the fraction of total sulfur deposition made up of dry deposition ( $F_D$ ) is less in eastern Canada (29%) than it is in eastern

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\*Prepared by L.A. Barrie

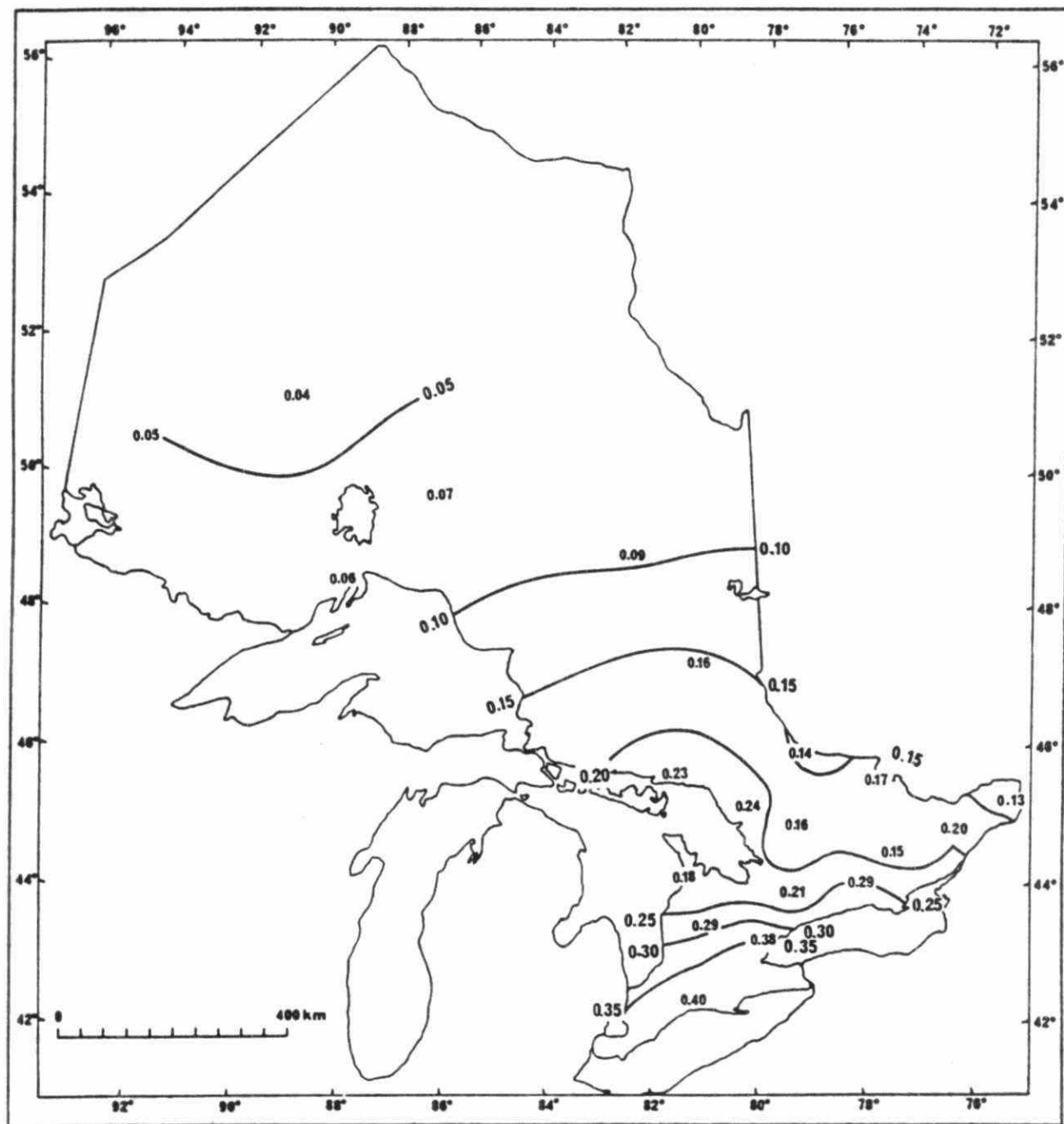


Figure 2.18 The annual dry deposition of total sulfur ( $\text{g S m}^{-2} \text{yr}^{-1}$ ) in Ontario in 1982.

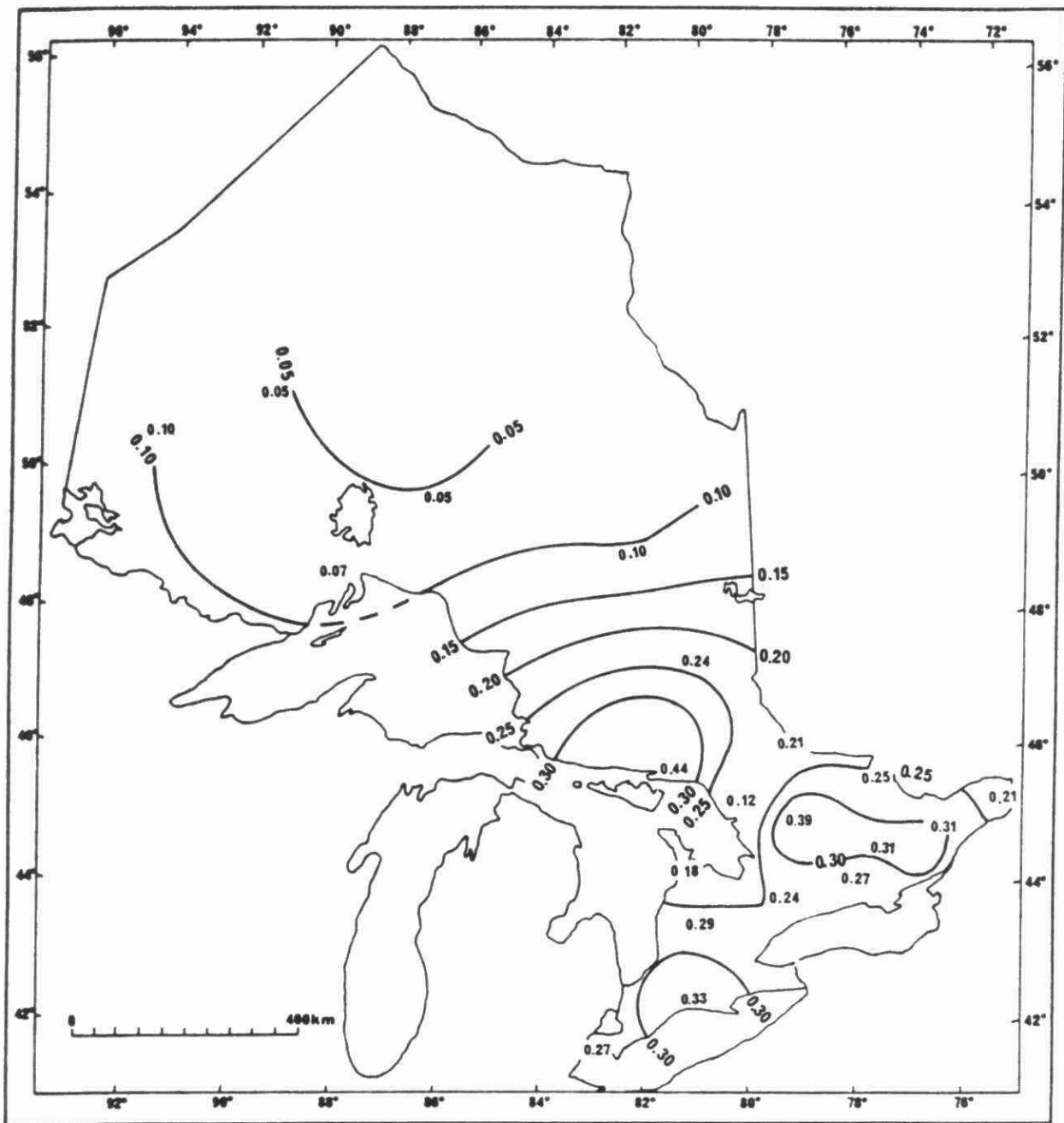


Figure 2.19 The annual dry deposition of  $\text{NO}_3$  ( $\text{g N m}^{-2}\text{yr}^{-1}$ ) in Ontario in 1982.



United States (57%). Logan (1984) has done a similar budget for nitrogen showing similar results.

More recent estimates of the relative importance of wet and dry deposition have been made for eastern Canada by Barrie and Sirois (1985) and in Ontario by Chan et al (1985). These are compared with the previous budget estimates in Table 2.6. The analysis by Barrie and Sirois shows a marked decrease in  $F_D$  for sulfur from 37% on the north shore of Lake Erie to less than 20% in more remote areas. The average  $F_D$  for the southern half of eastern Canada was 22%. The Ontario data is consistent with this picture showing a decrease in  $F_D$  from 40% in the extreme southwest falling off to 15-20% in the remote northern region. If one takes into account that  $F_D$  tends to decrease with increasing distance from sources, the estimate of  $F_D$  for sulfur in eastern Canada is closer to 20% than the 29% estimated by Whelpdale and Galloway. On the other hand, the estimate for nitrate by Logan is in fair agreement with current Canadian observations.

In the United States there are no routine regional air concentration measurements to use in confirming the budget estimates. There are however some isolated studies. In an area forested with mixed-oak woods Lovett and Lindberg found  $F_D$  for sulfate was 30% and for nitrate at least that much. In a study in Michigan, Dasch (1985) found that  $F_D$  was higher at the edge of a forest canopy than inside it. For dry oak  $F_D$  was 50% and 20% for nitrate and sulfate respectively at the edge of a canopy. Similarly for dry pine it was 58% and 13% respectively. Both these studies rely on canopy wash-off techniques which do not determine  $SO_2$  deposition. Thus the  $F_D$  estimates are lower limits.

Another way of estimating the relative importance of wet and dry deposition of sulfur is to do a mass balance study of a watershed. By comparing total outflow of sulfur with wet deposition and assuming that there is no net loss or storage of sulfur in the watershed with time, an estimate of the sum of fogwater deposition and dry deposition can be made. At Hubbard Brook in New Hampshire, the output of sulfate exceeded the measured input by about 40% with the difference attributed to dry deposition (Likens et al, 1977). Studies by Dillon et al (1982) on forested lake watersheds around Sudbury attributed 45 to 71% of the sulfate flowing out as being due to dry deposition or fogwater deposition. At Dorset, Ontario, further away from the major source of Sudbury, similar estimates made recently (Dillon personal communication) indicate that about 40% of the total deposition is not from precipitation. This is somewhat higher than the estimates made from air measurements by Chan et al (1985) for Dorset. Possibly fogwater deposition makes up the difference but also this could reflect an underestimate of current dry deposition estimates which use deposition velocities measured over homogeneous terrain in steady-state meteorological situations. Furthermore, there is no assurance as yet that the massive reservoir in the ecosystem is not changing with time causing and 'apparent' deposition that is not real. There is a need for further experimental studies to assess the usefulness of watershed mass balance as a technique for measuring non-precipitation atmospheric inputs of sulfates to complex terrain.

Table 2.6 The dry deposition as a percentage of the total estimated deposition obtained from several studies. (see text for details)

REGION	$\text{SO}_4$	$\text{NO}_3$
<u>BUDGET STUDIES</u>	%	%
Eastern North America	45	50
Eastern U.S.A.	57	59
Eastern Canada	29	23
<u>NETWORKS STATIONS</u>		
APN (Eastern Canada)	22	21
APIOS (Ontario)	16	38

#### 2.3.4. A Comparison of North American and European Air and Precipitation Quality, and Atmospheric Deposition Rates\*

Atmospheric deposition, as well as the direct impact of gaseous air pollutants, has been proposed as the cause of damage to aquatic ecosystems in Scandinavia and northeastern North America, as well as forests in several European countries (particularly Germany) and the United States. The purpose of this chapter is to compare air and precipitation quality, and atmospheric deposition, in Europe and North America.

Data will be compared primarily for the following:

- (1) precipitation concentrations and wet deposition of  $H^+$ ,  $SO_4^{=}$  and  $NO_3^-$ ; and
- (2) air concentrations of  $SO_2$  and  $O_3$ , pollutants which have been implicated in the "novel forest decline" problem (Krause et al., 1985; Ashmore et al., 1985).

Also of interest are the dry deposition of sulfur and nitrogen compounds, and wet and dry deposition of trace metals. Relatively little information is available on these components of the atmospheric input, although the dry deposition pattern should roughly follow the air concentration pattern, and in the heavily polluted areas of central Europe and northeastern North America, one can say that dry deposition rate of sulfur and nitrogen compounds could equal or exceed the wet deposition rate. McLaughlin (1985) gives a limited comparison of atmospheric deposition for four trace metals at some rural eastern U.S. locations and the Solling forest in West Germany, which indicates substantially higher (two-fold or more) deposition at the West German site. Another type of atmospheric input where information is presently very limited is that due to fogs and low clouds. Many of the forested areas of Europe and eastern North America are on elevated terrain and frequently in contact with mountain fogs. Pollutant concentrations in fog, and cloud droplets, can be relatively high, leading to deposition rates that could potentially be a significant portion of the total atmospheric deposition (Summers et al., 1985; Fowler et al., 1985; Krause et al., 1985; Lovett, 1982). It has also recently been suggested that dissolved hydrogen peroxide (in clouds and fogs) can have a direct impact on vegetation leading to damage similar to that observed in some of the forested areas of concern (Slalina et al., 1985). Very few data are available on actual measured inputs from fogs and low clouds, although this is an area of much current research. McLaughlin (1985) cites some data on fog and cloudwater concentrations in southern Germany and the northeastern United States, which suggest higher levels (except for acidity) in the former area, but there is at present insufficient information to draw any general conclusions.

##### 2.3.4.1 Precipitation Chemistry and Wet Deposition

(a) Precipitation pH: The acidity of precipitation in Europe and North America, expressed as pH, is compared in Figures 2.20(a) to (c). The European data are averages over the period 1978-1982, and were taken from EMEP (1984). The North

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\*Prepared by M.A. Lusiis and H. Dovland

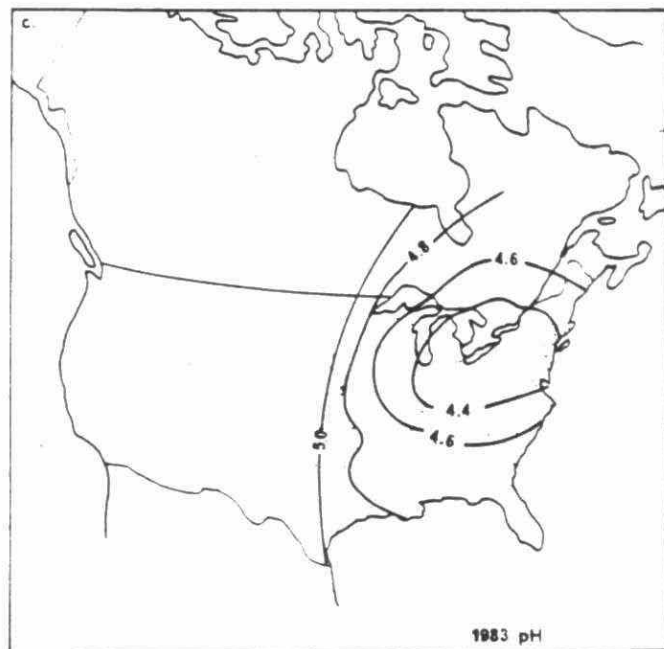
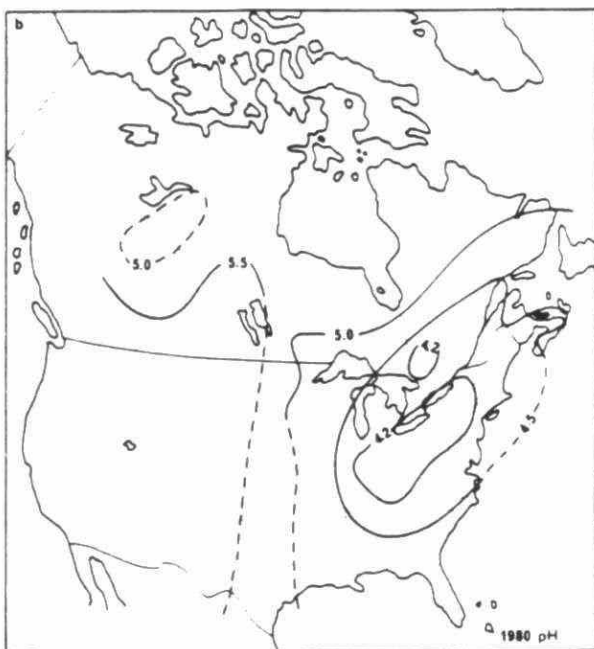
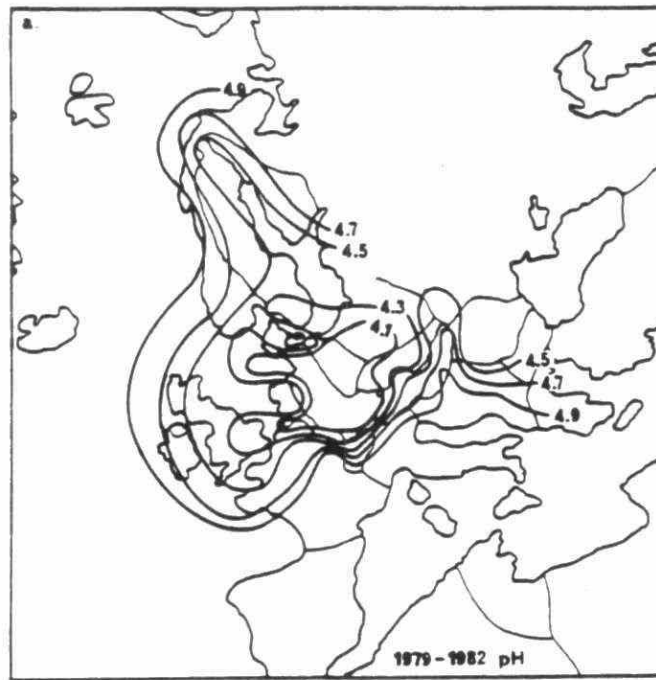


Figure 2.20: Comparison of Precipitation pH Values in Europe (a) and North America (b and c).

American data are shown for two years - 1980 and 1983, to give an indication of the year-to-year variability (see also Summers et. al., 1985). The data for 1980 are from MOI (1982), while the 1983 data are from Olsen and Slavich (1985). An examination of the North American and European pH data suggests that comparable values are encountered in the highly impacted areas of Europe (Germany, Belgium and The Netherlands) and North America (the lower Great Lakes), with long-term average pH values near 4.1.

(b) Precipitation Sulfates: Figures 2.21(a) to (c) compare precipitation sulfate concentrations in Europe and North America, and were taken from the same sources as the pH data in the above paragraph. It appears that sulfate concentrations in central and eastern Europe (generally greater than 6 mg  $\text{SO}_4/\text{l}$ ) exceed those in the most heavily impacted North American area, i.e., the lower Great Lakes (where sulfate levels are somewhat above 3 mg  $\text{SO}_4/\text{l}$ ). Figures 2.22(a) and (b) compare sulfate wet deposition in Scandinavia (Semb and Dovland, 1985) and eastern North America (Summers et al., 1985) for 1983. Note that the wet deposition levels observed in southern Scandinavia (20-40 kg  $\text{SO}_4 \text{ ha}^{-1} \text{ y}^{-1}$ ), where detrimental effects have been documented on the aquatic ecosystem for many years, now occur over large areas of eastern North America (the 20 kg  $\text{ha}^{-1}$  contour line roughly follows the Mississippi River, then bends northeast across central Wisconsin). It may also be noted that in southern Germany, long-term sulfate wet deposition levels in the range 50-70 kg  $\text{ha}^{-1} \text{ y}^{-1}$  are reported by EMEP (1984).

(c) Precipitation Nitrates: A comparison of precipitation nitrate concentrations in Europe and North America is based on Figures 2.23(a) to (c), taken from the same sources of information as in paragraph (a). As with sulfate concentration and deposition values, nitrates also show a considerable year-to-year variation (compare Figures 2.23(b) and (c)). The available information suggests that the area of high nitrate levels in precipitation (greater than 2 mg  $\text{NO}_3/\text{l}$ ) is somewhat greater in Europe than North America. The same observations are expected to apply to deposition.

(d) Nitrate/Sulfate Ratio in Precipitation: Figures 2.24(a) (Fowler et al., 1985) and (b) (Summers and Barrie, 1985) compare sulfate and nitrate levels in Europe and North America. Clearly, nitrate is an important contributor to precipitation acidity on both continents.

#### 2.3.4.2 Air Concentrations and Dry Deposition

(a) Sulfur Compounds: There are relatively few measurements of particulate sulfur and sulfur dioxide at rural North American sites. Data from the SURE program are used here, although they only span two years (1977 and 1978). More data are available from the European EMEP program, as shown in Figures 2.25(a) and (b) (EMEP, 1984), over the 1978-1982 period. Figure 2.26(a) shows the 50th percentile of the hourly  $\text{SO}_2$  measurements (from August 1977 through July 1978) at the EPRI/SURE stations. Similar information for daily average respirable sulfates, from the "seasonal" months October 1977, and January, February, April and July 1978, is shown in Figure 2.26(b) (EPRI, 1983). A comparison of the European and North American data suggests that concentrations of airborne sulfur oxides (and hence, probably dry deposition rates also) are somewhat greater in central Europe than the impacted areas of eastern North America. However, it must be

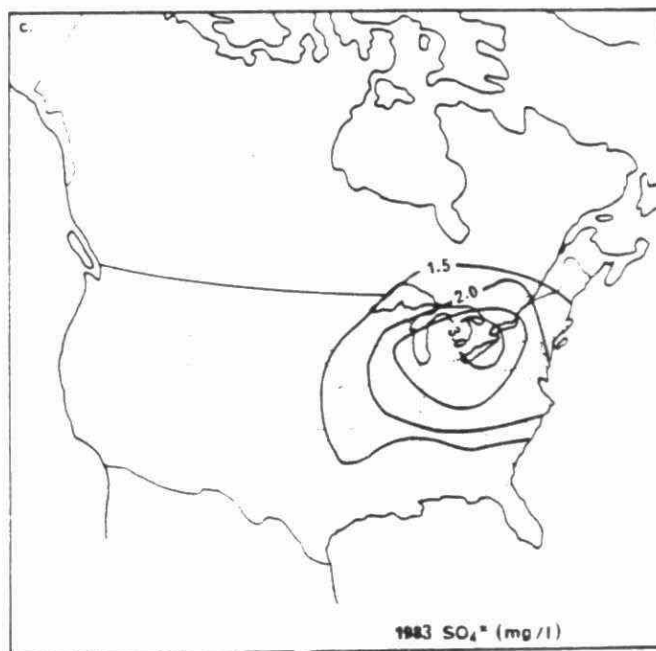
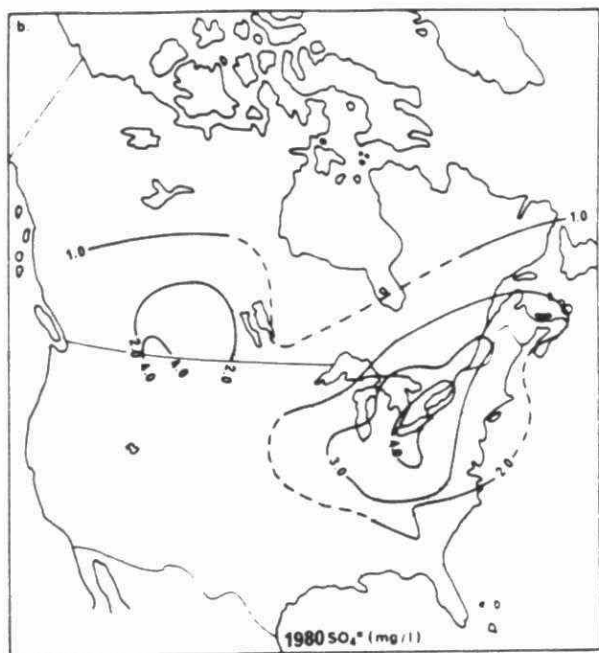
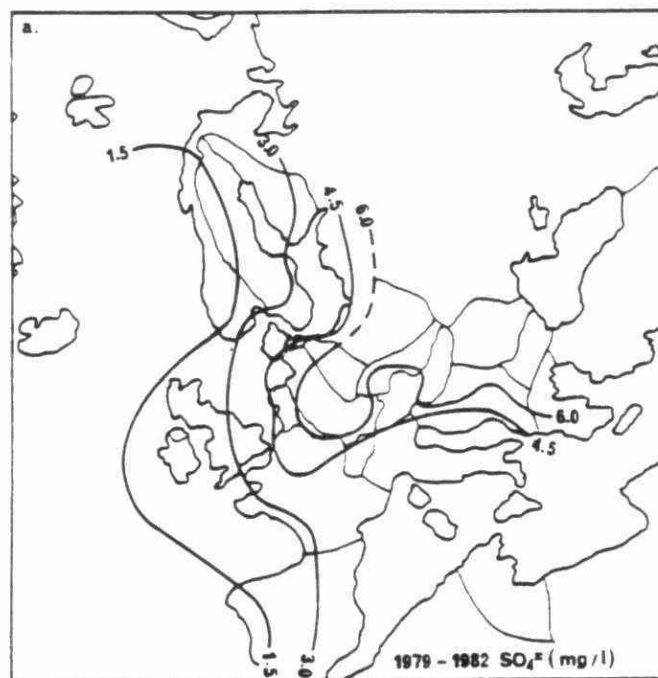


Figure 2.21: Comparison of Precipitation Sulfate Levels in Europe (a) and North America (b and c).

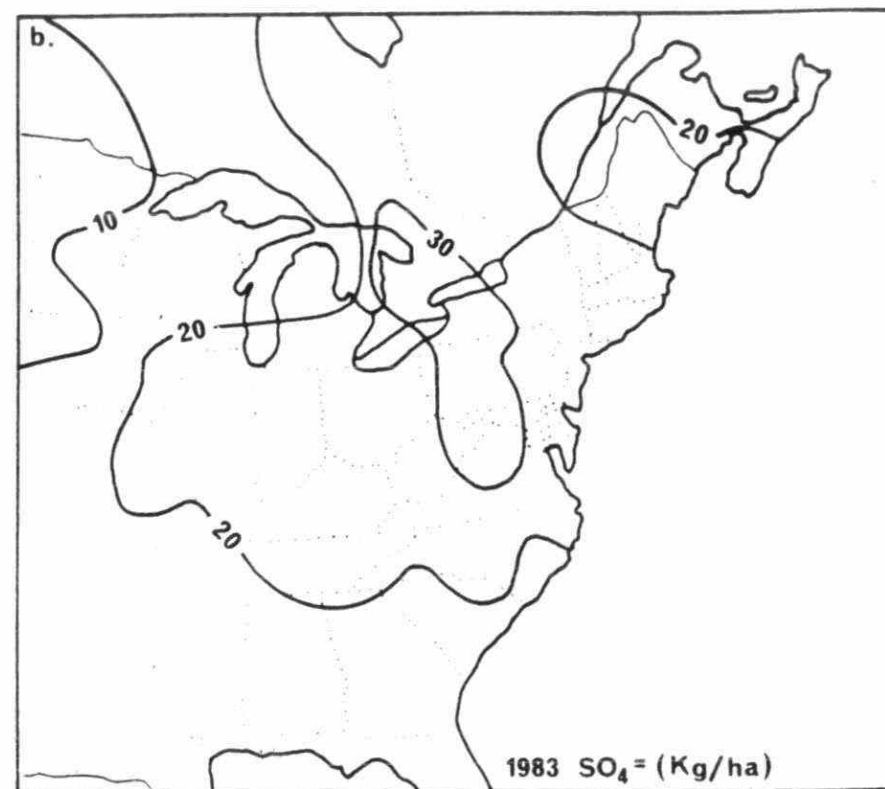
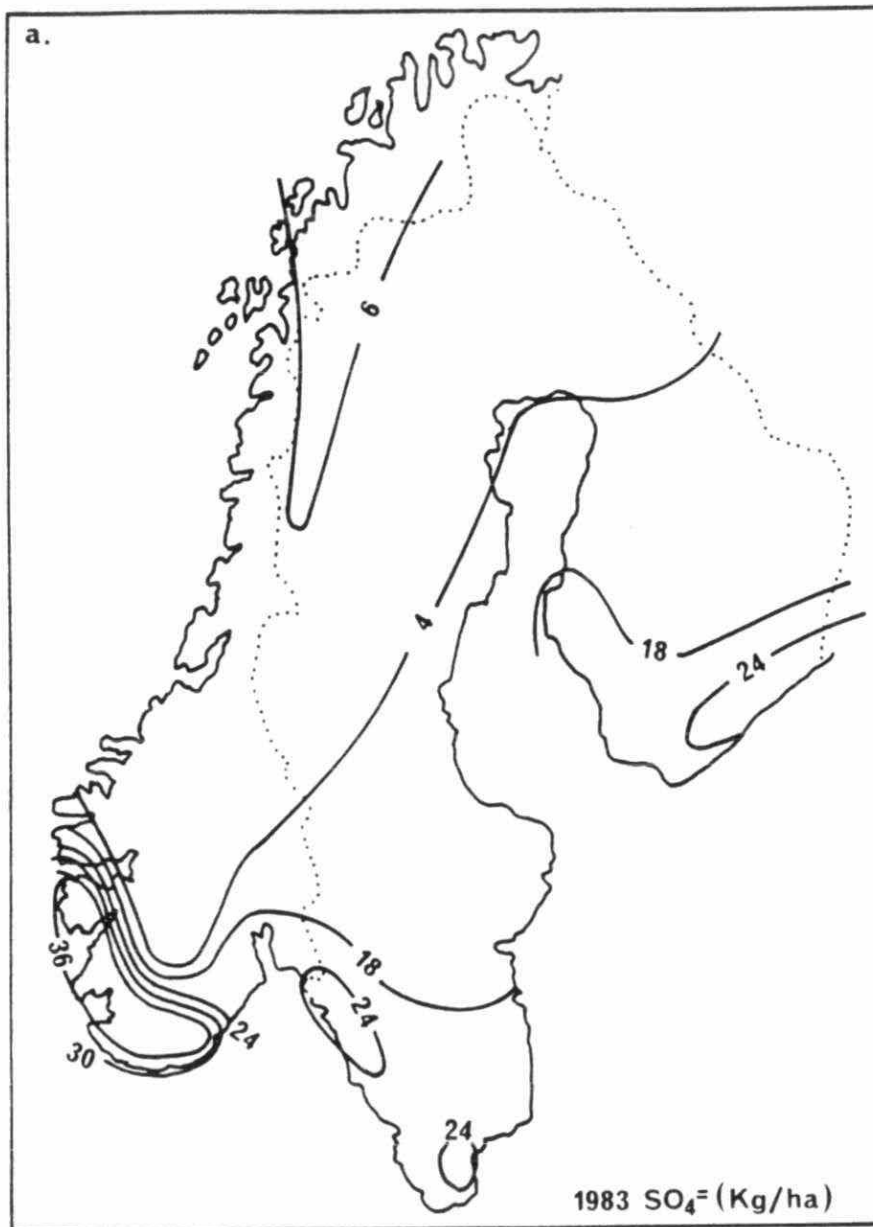


Figure 2.22: Comparison of Sulfate Wet Deposition Rates in Scandinavia (a) and Eastern North America (b).



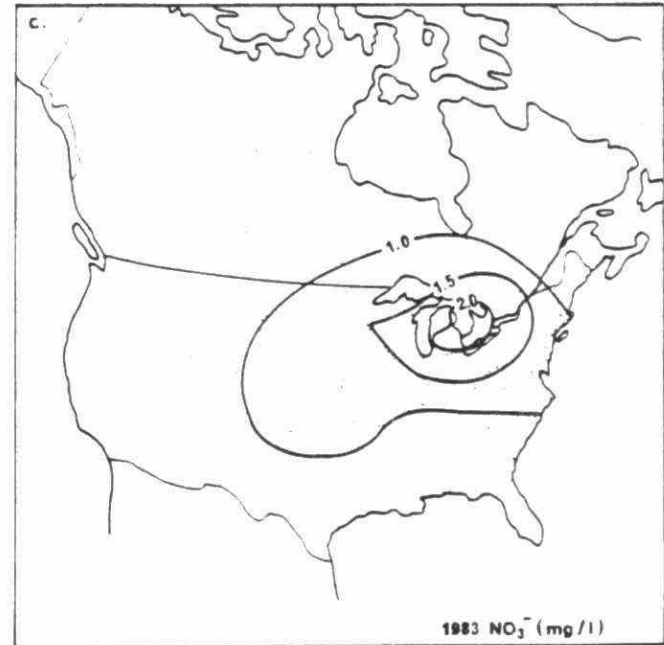
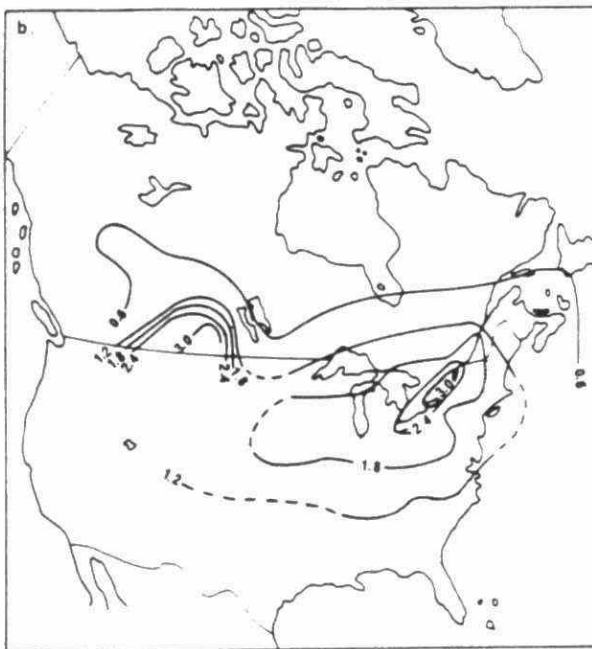
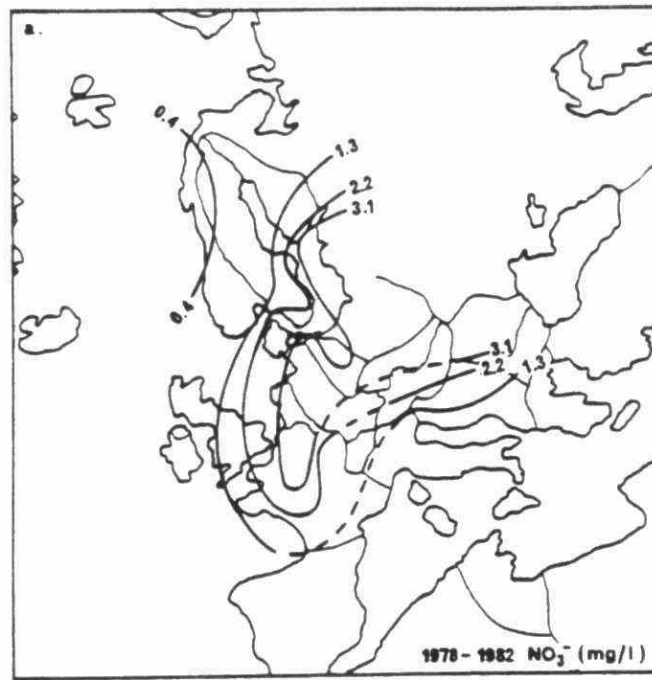


Figure 2.23: Comparison of Precipitation Nitrate Levels in Europe (a) and North America (b and c).



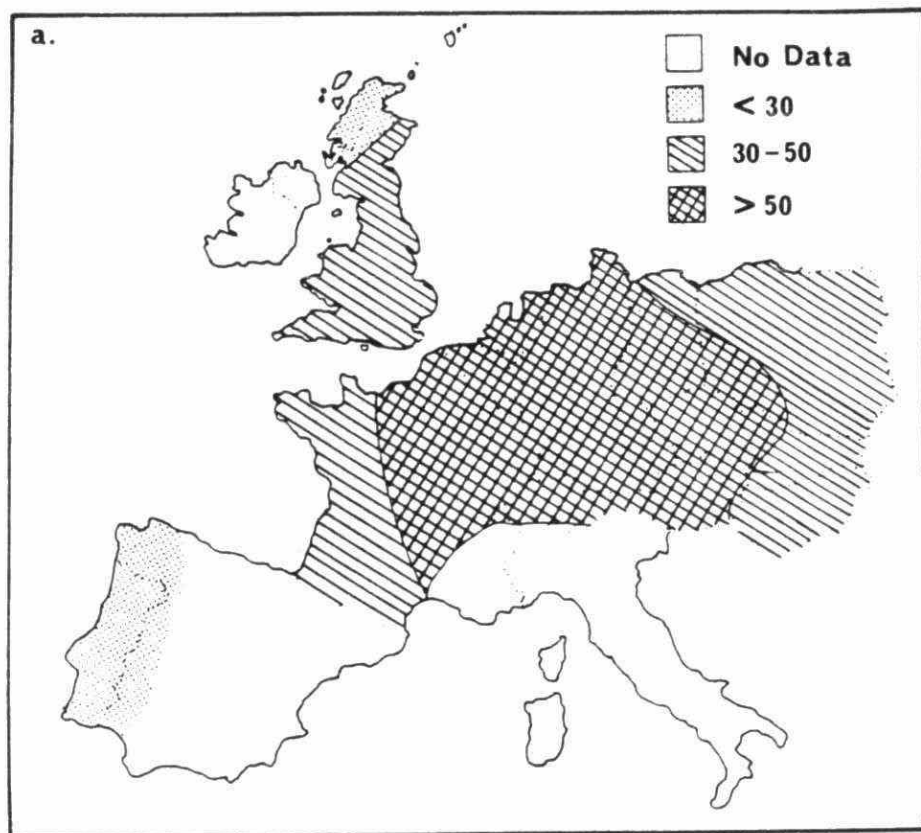


Figure 2.24: Comparison of Nitrate/Sulfate Equivalent Ratios (%) in Europe (a) and Eastern North America (b).

remembered that near strong emission areas,  $\text{SO}_2$  concentrations may have short-term excursions to levels where direct damage may result, especially in conjunction with elevated ozone levels. Excursions to levels in excess of  $500 \mu\text{g SO}_2 \text{ m}^{-3}$  have been encountered in areas of Bavaria, Poland, the German Democratic Republic and Czechoslovakia (Krause et al., 1985). Figures 2.25(a) and 2.26(a) do not include any information on short-term concentration excursions, but the SURE data (EPRI, 1983) suggest that hourly levels of this magnitude are very rare in the rural northeastern United States.

(b) Ozone: Information on ozone is not readily available on a directly comparable basis. Relatively little monitoring has been carried out at rural locations. Fowler et al. (1985) have presented data on the number of hours during which ozone concentrations exceed 75 ppb (a level regarded as generally phytotoxic) in Europe using data from the period 1978-1983. Their results are shown in Figure 2.27(a). Scandinavian data expressed in a comparable manner were not available, although ozone episodes having hourly average concentrations in excess of 100 ppb have been reported in Sweden and Norway (Grennfelt and Schjoldager, 1984; Semb and Dovland, 1985). For comparison, we include Figure 2.27(b), which shows the mean number of exceedances per year of the 80 ppb hourly average at the eastern U.S. National Air Pollution Background Network sites and some sites in Ontario and Nova Scotia, as determined over at least three years (at most sites, five years or more) during the period 1976-1984 (Evans, 1985; Kiely, 1985; Moores, 1985). Note that the values shown in southern Ontario are a composite of results from several rural stations in the area, while the Nova Scotia results are based primarily on data available for the May-September period (no exceedances have been observed in the available data for other months).

Figures 2.27(a) and (b) are for slightly different hourly average levels (75 as compared to 80), and the data base is sparse. Nevertheless, the figures suggest that larger areas of Europe (especially southern and central Germany and southern France) are exposed to harmful ozone levels than is the case in North America. However, there are several qualifications attached to this comparison:

- (1) Altitude effects are not considered. As discussed by Fowler et al. (1985), average concentrations of ozone increase with altitude, and the impact at high altitudes may be considerably different from that at low altitude.
- (2) Detailed information on the European site locations and monitoring methods is not available. While the U.S. data come from remote monitoring sites located at National Forests, there may well be data in Figure 2.27(a) from rural European sites located near urban or industrial areas. As data from both Europe and North American clearly show (e.g. Cleveland and Graedel, 1979; Guderian, 1984; Kelly et al., 1985), nearby urban/industrial areas can have a pronounced impact on rural ozone levels, during the summer months.

It is therefore of interest to compare the available data for one particular region, namely southern Germany, where forest damage has been most dramatic, with the North American observations. This has been recently done by Ashmore et al.

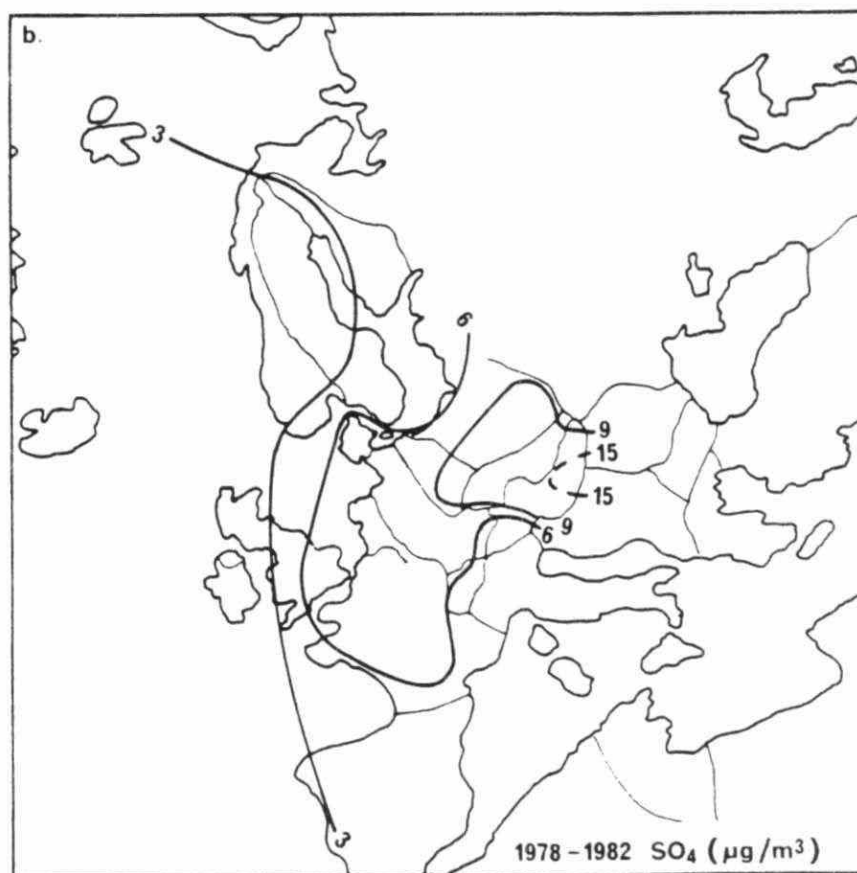
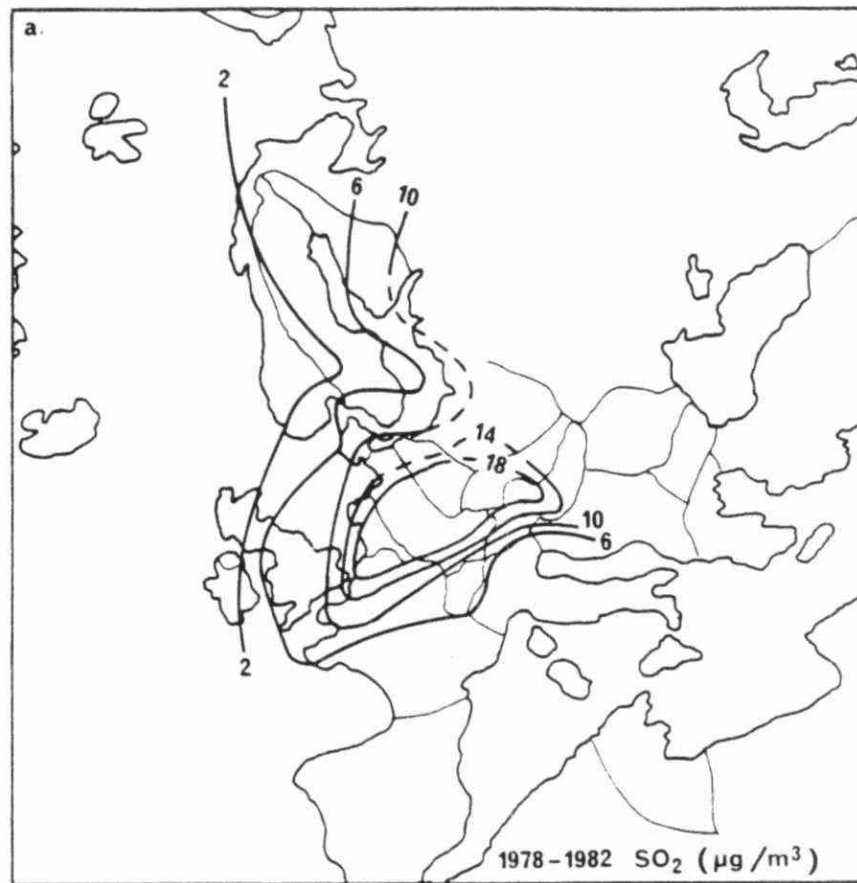


Figure 2.25: Airborne Sulfur Dioxide (a) and Particulate Sulfate (b) Levels in Europe.

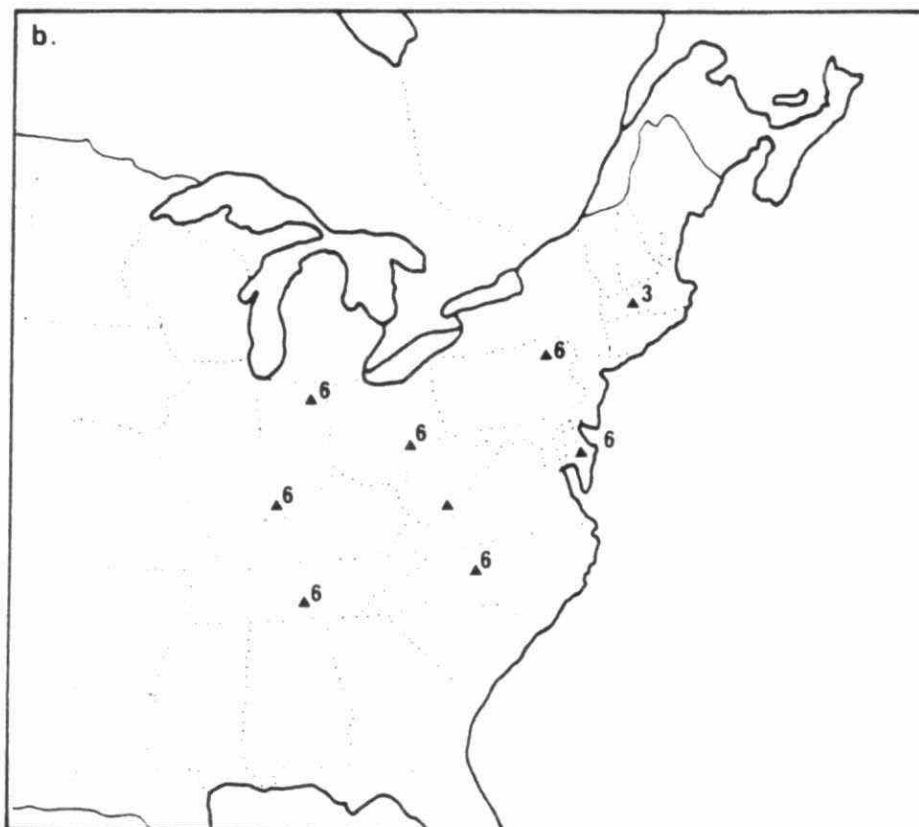


Figure 2.26: Airborne Sulfur Dioxide (a) and Particulate Sulfate (b) Levels in Eastern North America.

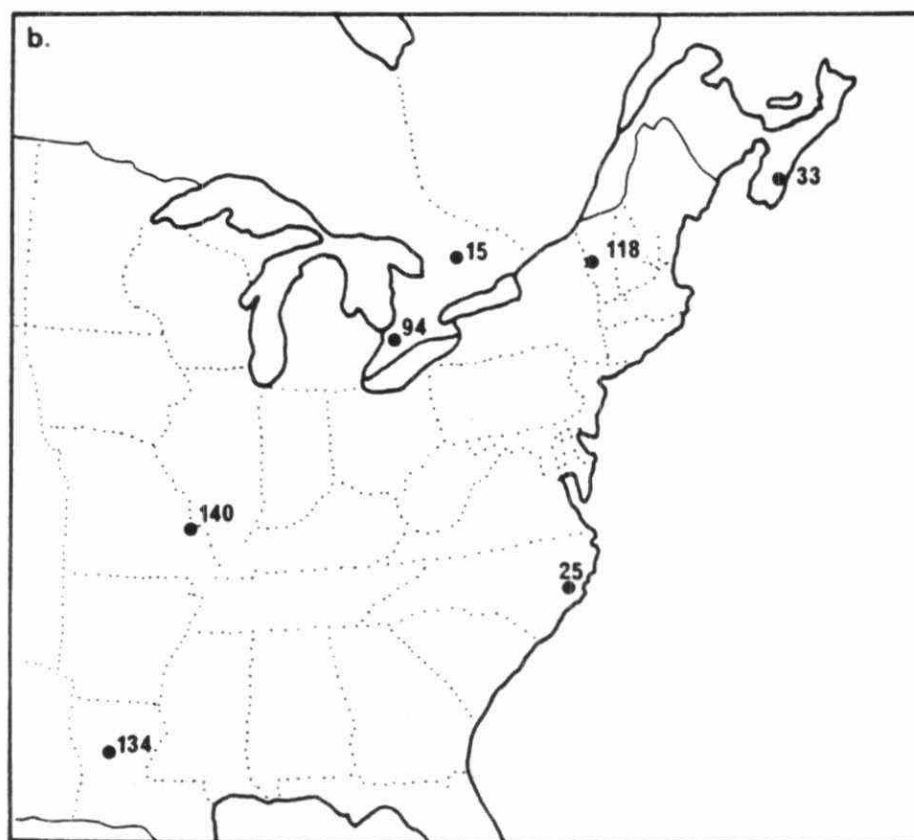
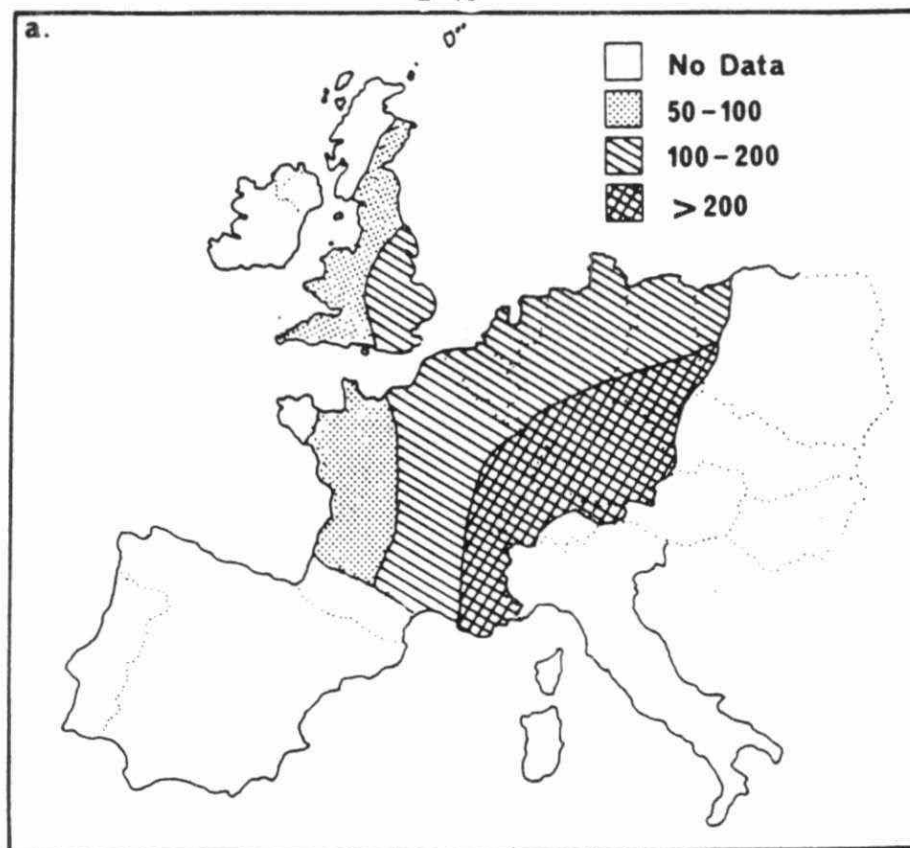


Figure 2.27: Comparison of Hours per Year in which Ozone Exceeds 75 ppm in Europe (a) and 80 ppb in Eastern North America (b).

(1985), who found that concentrations of ozone are quite similar in areas where forest damage has been documented and ozone data exist. The mean summertime concentrations are about 50 ppb, while concentrations above 100 ppb occur in up to three to five percent of summer hours. McLaughlin (1985) also carried out a broad comparison of ozone levels in the Federal Republic of Germany and various sites in the USA and found the same general concentration ranges. In the forested areas of southern Germany, maximum hourly values in the 100-180 ppb range have been observed (McLaughlin, 1985; Ashmore et al., 1985), while at the National Forest sites in eastern USA, maximum concentrations have generally been in the 100-150 ppb range (Evans, 1985). However, the available data (Figure 2.27(b)) suggest a fairly rapid drop-off in non-urban ozone levels to the north of the US-Canada border, with the occurrence of photochemical ozone events in forested areas of Canada being a fairly rare phenomenon.

#### 2.3.4.3. Summary

A comparison has been carried out of the available air and precipitation data in Europe and eastern North America. This comparison has not been extensive, and, due to lack of data, has been somewhat incomplete for dry deposition of sulfur and nitrogen compounds, as well as the potentially important question of fog and cloudwater chemistry at high-elevation sites. The precipitation data show comparable levels of acidity (pH about 4.1) in the areas of maximum industrial impact (central Europe and lower Great Lakes area). Sulfate and nitrate concentration and wet deposition rates are somewhat greater in central and eastern Europe than in North America, but much of eastern North America, east of the Mississippi River, receives sulfate wet deposition levels comparable to those observed in southern Scandinavia (i.e., 20-40 kg SO<sub>4</sub> ha<sup>-1</sup> y<sup>-1</sup>). The available data show that nitrates are an important contributor to precipitation acidity on both continents.

Air concentrations of sulfur oxides are somewhat greater in central Europe than eastern North America, and the available information suggests that short-term elevated values are more common, especially in parts of central and eastern Europe. For the nitrogen oxides, there is insufficient information to make a meaningful comparison.

The available data suggest roughly comparable ozone levels in portions of the eastern United States and Europe (e.g. the Appalachians, southern Germany) where forest damage has been observed. However, the area affected by high ozone levels seems to be somewhat more extensive in Europe: in eastern North America, there is a fairly rapid decrease in rural ozone levels to the north of the US-Canada border, and based on the available data, high ozone concentrations are a rare occurrence in the forested areas of Canada.

Table 2.7 summarizes air and precipitation quality, and atmospheric deposition data at, or in the vicinity of, a number of receptor sites in Europe and North America, which are of current interest (southern Germany and Scandinavia, the Appalachians and Muskoka-Haliburton). While the specific observations in Table 2.7 generally are in accord with the statements made earlier, one should bear in mind the following points:

1. The database is still very limited, especially for air quality in

rural North America sites. For this reason, it was often not possible to get exactly co-located, long-term measurements, but data from nearby sites had to be used. Also, the measurement periods vary from one to several years.

2. The table does not fully address extreme values, which may play an important role in environmental damage, especially to forests, nor does it deal with the question of input due to fogs, which could be substantial at the high-altitude sites. The level of exposure to ozone is also a function of the altitude (Fowler, 1985).
3. The information on trace metals deposition, and dry deposition, is very incomplete, and may be inconsistent. For example, it is not clear why there should be such a large difference in the cited sulfur dry deposition rates, based on the ambient sulfur dioxide and sulfate levels shown at the different sites in Table 2.7.

Table 2.7 does, however, suggest that:

1. Levels of  $\text{SO}_2$  and  $\text{O}_3$  are somewhat greater in southern Germany. A higher frequency of elevated ozone concentrations is also suggested in the data.
2. Long-term precipitation acidity levels are comparable at all the sites.
3. Sulfate wet deposition is in excess of the target  $20 \text{ kg ha}^{-1} \text{ y}^{-1}$  proposed for protecting sensitive aquatic systems at all the sites.
4. Generally, wet deposition of sulfates, nitrates and trace metals is higher in southern Germany than in the southern Scandinavian or North American Sites.

Table 2.7: Comparison of Air and Precipitation Quality and Atmospheric Deposition at European and North American Sites (see also footnotes on following page)

Parameter	S. Germany	S. Scandinavia	Muskoka-Haliburton	Southern	Appalachians Area Central	Northern
SO <sub>2</sub> (ug m <sup>-3</sup> )	10-20 (ann. mean) <sup>1,2</sup> 500 (short term peak) <sup>2</sup>	6-10 <sup>5</sup>	39	314 26 (hourly average, 90 percentile)	517 6017 (hourly average, 90 percentile)	
O <sub>3</sub> (ppb)	50 (summer mean) <sup>3</sup> >100 (for 5 % summer hrs.) <sup>3</sup> >75 for >200 h per year <sup>4</sup>	>80 for 50 h per year <sup>23</sup>	2610 >5810 >80 for 15 h per year <sup>10</sup>	4518 >7518 >80 for 140 h <sup>18</sup>	not avail.	3321 >6721 >80 for 118h <sup>21</sup>
SO <sub>4</sub> (ug m <sup>-3</sup> )	4-7 <sup>5</sup>	3-6 <sup>5</sup>	39	614	517	
Precip. pH	4.1 <sup>5</sup>	4.3 <sup>5</sup>	4.2 <sup>11</sup>	4.2-4.3 <sup>15</sup>	4.0 <sup>19</sup>	4.2 <sup>20</sup>
SO <sub>4</sub> Deposition (kg ha <sup>-1</sup> y <sup>-1</sup> )						
Wet	40-100 <sup>6</sup>	20-40 <sup>8</sup>	2811	3415	4719	2820
Dry	24 <sup>1</sup>		512	4415	2822	
NO <sub>3</sub> Deposition (kg ha <sup>-1</sup> y <sup>-1</sup> )						
Wet	20-70 <sup>6</sup>	20-35 <sup>5</sup>	2011	1215	3619	2020
Dry	18 <sup>1</sup>		1712	2015	not avail.	not avail.
Trace Metals Deposition (total, mg m <sup>-2</sup> y <sup>-1</sup> )						
Cd	1.6-2.0 <sup>7</sup>	0.3 <sup>23</sup>	0.5 <sup>13</sup>	0.5 <sup>16</sup>	not avail.	not avail.
Mn	-	-	1013	2216		
Pb	44-73 <sup>7</sup>	823	2013	1516		
Zn	163-173 <sup>7</sup>	1023	-	8.9 <sup>16</sup>		

2-48



## Footnotes for Table 2.7

1. Fowler et al. (1985). Dry deposition estimated from air concentrations.
2. Cited by Krause et al. (1985), for Black Forest.
3. Cited by Ashmore et al. (1985).
4. Fowler et al. (1985). This applies to low elevation sites. For high elevation sites, the number of hours in excess of 75 ppb is larger.
5. 1978-1982 average, EMEP (1984).
6. Cited by Fowler et al. (1985). The lower values refer to low altitude sites. The higher values are more typical of high altitude sites. Additional inputs due to cloudwater interception (not shown) at high altitude sites could be significant.
7. Cited by McLaughlin (1985) for Solling, Germany.
8. Semb and Dovland (1985).
9. 1982-83 mean, Ontario Ministry of the Environment Reports ARB-165-84—ARSP and ARB-089-85-AQM.
10. P. Kiely, private communication based on Ontario Ministry of the Environment Database, average for 1981-1984.
11. 1981-83 mean, Ontario Ministry of the Environment Reports ARB-102-85-ARSP, ARB-110-84-ARSP and ARB-087-85-AQM.
12. 1982 value, Chan et al. "Air Concentration and Dry Deposition Fields of Pollutants in Ontario" (in Press). Dry deposition estimate from air concentrations.

13. Jefferies, D. and Snyder, W.R. (1981) "Atmospheric Deposition of Heavy Metals in Central Ontario", Water Air and Soil Poll., 15, 127-152.
14. 1977-78 data for EPRI/SURE Giles County Station, from EPRI (1983).
15. S. Lindberg, data for Walker Branch Watershed, to be published in Science. Dry deposition from micrometeorological measurements.
16. Cited by McLaughlin (1985) for Walker Branch Watershed.
17. 1977-78 data for EPRI/SURE Scranton Station, from EPRI (1983).
18. No local measurements were available. The data shown are taken from the Mark Twain National Air Pollution Background Network site in Missouri, 1979-1983. (Evans, 1985).
19. From MAP3S network, for Penn State site, 1977-79, See Atmos. Environ., 16, 1603-1631 (1982).
20. From MAP3S network, for Whiteface Mountain site, 1977-79, same reference as in 19 above.
21. Evans (1985), data for Green Mountain National Air Pollution Background Network site in Vermont, 1977-1982.
22. Estimated from the air concentration data, using a deposition velocity of 0.4 and 0.2 cm s<sup>-1</sup> respectively for SO<sub>2</sub> and SO<sub>4</sub> (Voldner and Sirois, 1985).
23. Data provided by Norwegian Institute for Air Research (NILU).

## 2.4 OBSERVED CHANGES IN PATTERNS IN THE LAST 30 YEARS

### 2.4.1 Precipitation Chemistry\*

Awareness of the crucial importance of high quality, long-term data sets for trend detection and analysis has increased tremendously since the time of the Memorandum of Intent work. Unfortunately, despite repeated attempts to determine trends in available precipitation composition data, we are still confronted with the problem of poor quality records prior to about 1980. As a consequence, conclusions regarding changes in spatial distributions or temporal trends during the past 30 years remain rather tenuous.

The U.S. National Academy of Sciences has recently completed a comprehensive review of trends in environmental data related to the acid deposition issue (NAS, 1986). The portion of the report dealing with precipitation chemistry reviewed available publications which dealt with analyses of the data sets shown in Figure 2.28. Rather than reproduce much of the content of the NAS report, the conclusions pertinent to the present assessment are presented below.

Perhaps the most conclusive evidence of regional-scale acidification in eastern North America is that the eastern half of the United States and southeastern Canada south of James Bay experience concentrations of sulfate and nitrate in precipitation that are, in general, greater by at least a factor of five than those in remote areas of the world. Thus concentrations must have increased by this amount in northeastern North America since some time prior to the 1950s.

Precipitation chemistry data prior to 1955 are too unreliable to be used for trend analysis. It is clear, however, that precipitation is currently more acidic in parts of the eastern United States than it was in the mid-1950s or the mid-1960s. The exact amount of this change and the relative importance of contributing factors, such as anthropogenic sources of acidic constituents, natural dust sources and changed sampling protocols have not yet been (and may never be) determined. Increases in precipitation-sulfate and hydrogen ion concentrations since the mid-1950s are most confidently linked to human activity in the southeastern United States.

The few longest continuous records, unfortunately, are from bulk collection. At Hubbard Brook in New Hampshire, general agreement exists among several reports for the magnitude and direction of trends since 1964 in some species: hydrogen ion shows no overall significant trend; sulfate has decreased at approximately two percent per year; sodium, chloride, calcium, magnesium and potassium have shown strong decreases with time; nitrate appears to have increased until about 1970/71 and then levelled off; the analyses for ammonium are contradictory. Past analyses of the USGS bulk data from New York and Pennsylvania since the mid-1960s do not yield a consistent network-wide trend for the acid-related (or other) species. The stations at Mays Point and Hinckley, which do have the most

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\*Prepared by D.M. Whelpdale

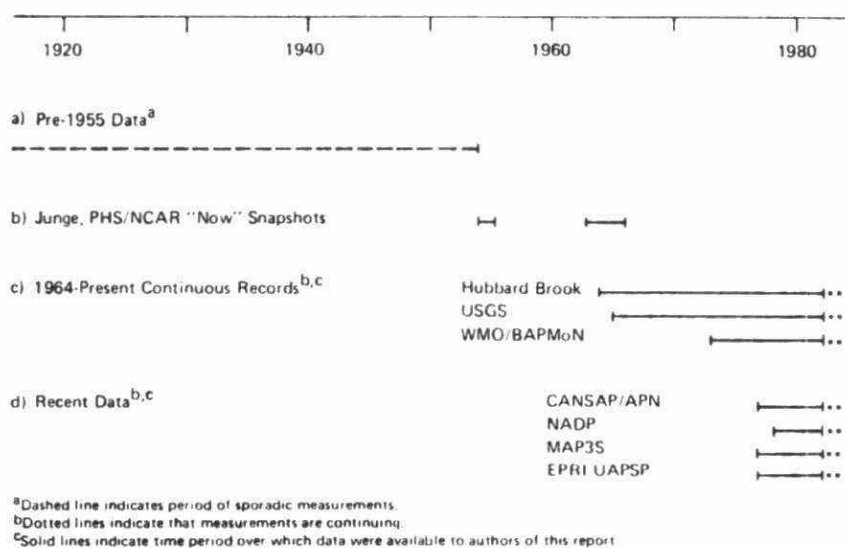


Figure 2.28 Summary of available precipitation chemistry data bases.

[Source: NAS, 1986]

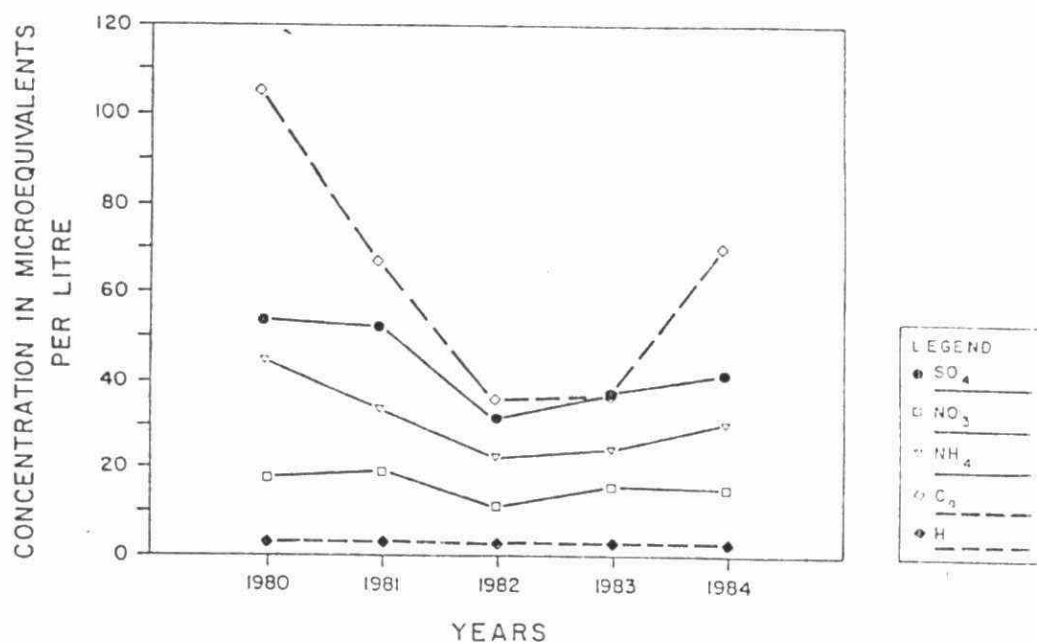


Figure 2.29 Temporal profile of precipitation quality in Alberta for the period 1980-1984

[Source: Bertram et al., 1985]

complete records, show sulfate trends consistent with that at Hubbard Brook, thus lending more confidence to the regional nature of the sulfate trend.

Preliminary analyses of the CANSAP-APN and NADP data for the eastern half of the continent, for the period 1979-1982, do not readily reflect changes that occurred in anthropogenic emissions. Concentration changes from year-to-year occur coincidentally in both anthropogenic ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ) and natural ( $\text{Ca}^{++}$ ) constituents, indicating that meteorological rather than emission influences dominated during this period.

One of the most important conclusions from the NAS report was that the spatial distributions of annual (precipitation-weighted-mean) concentrations and wet deposition for the major ionic species in precipitation are adequately known on the regional to continental scale in North America to afford comparison with spatial patterns of emissions and other possible indicators of acid deposition, such as visibility and the quality of surface waters. The 1980 concentration and deposition fields are acceptably representative of the broad-scale patterns present in the seven-year period 1977-1983.

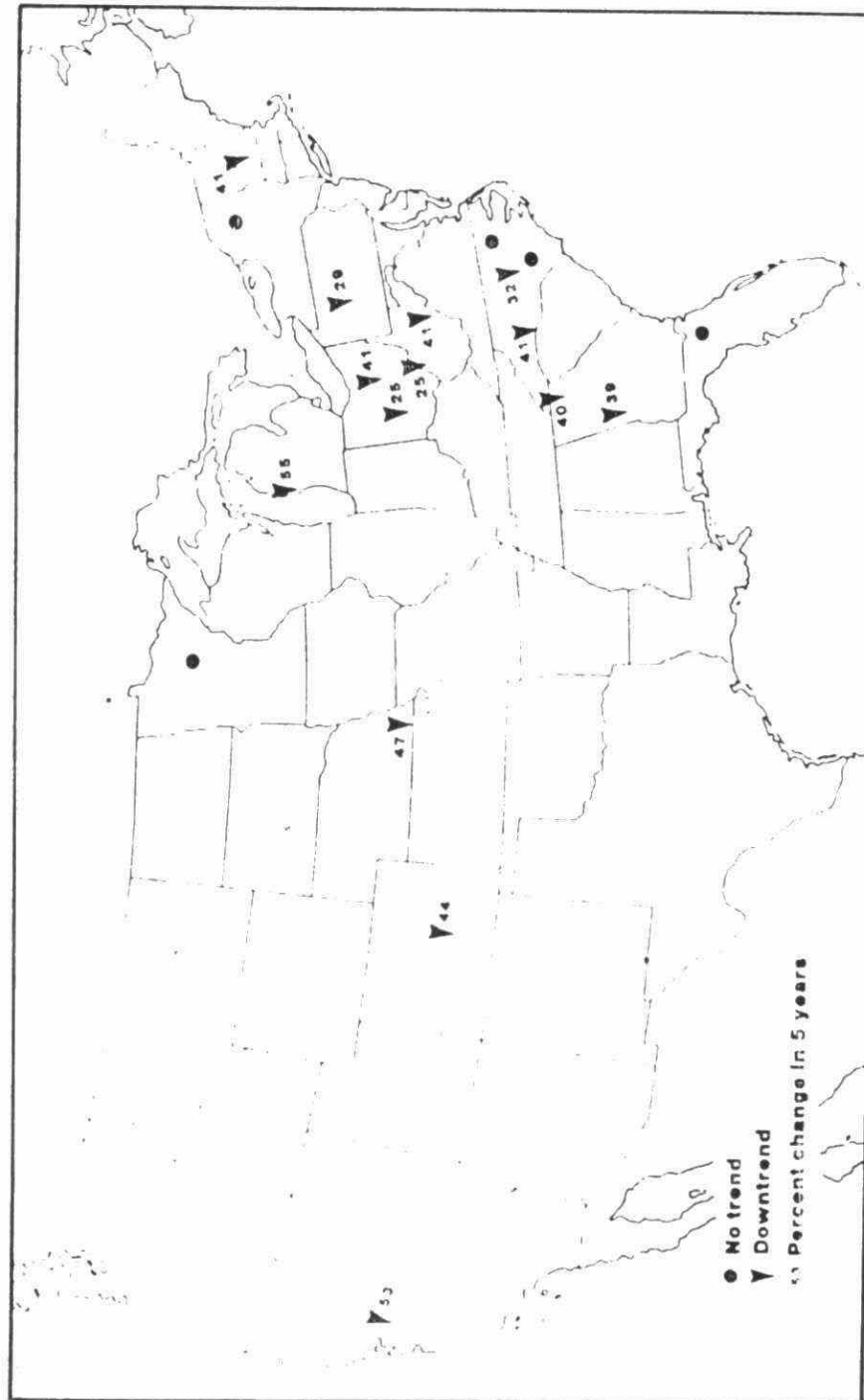
Presentations at the Muskoka '85 Conference provided information on recent changes in parts of Canada and the United States. Alberta Environment data for the period 1980-1984 (Bertram et al., 1985) do not show overall trends for concentrations of  $\text{H}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  or  $\text{NH}_4^+$  (Figure 2.29). They do, however, provide valuable information on the variability of precipitation data. A lengthy record of bulk precipitation samples (1970-1984) at ELA (Linsey and Schindler, 1985) shows an increase in acid-related species after 1982:  $[\text{H}^+]$  increased from 8-14 to 47  $\mu\text{eq l}^{-1}$  (annual average), and the deposition of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$  and  $\text{H}^+$  almost doubled after 1982 compared with earlier years. These increases have been attributed to increased frequencies of episodes of more polluted precipitation rather than to increased emissions. Analysis of data from five rural sites in Nova Scotia between 1978 and 1984 (Underwood, 1985) shows temporal changes. 1980 was found to be the most acidic year of the period, and the deposition of  $\text{SO}_4^{2-}$ , (corrected for sea-salt)  $\text{NO}_3^-$  and  $\text{H}^+$  appear to have decreased in the more recent years. As an example, the time regression of  $\text{SO}_4^{2-}$  is

$$\text{SO}_4^{2-} [\text{kg ha}^{-1}] = -0.88y + 20.07 \quad (r^2 = 0.20, N=31)$$

The data presented for Kejimikujik, Nova Scotia by Barrie and Sirois (1986) are not inconsistent with this trend.

Recent analysis (Pickering and Kapinos, 1985) of data from 19 weekly precipitation monitoring stations in the National Atmospheric Deposition Program and National Trends Network with five or more years of record from 1978 to 1983 has revealed a number of statistically significant trends in  $\text{SO}_4^{2-}$ . Of the 19 stations, five had no trends and 14 showed downtrends ranging from 25 to 55% during the five-year period (Figure 2.30).  $\text{NO}_3^-$  showed downtrends at 12 stations, no trends at five stations and uptrends

# TRENDS IN SULFATE CONTENT OF PRECIPITATION-1978-83



Trends in volume-adjusted concentrations of sulfate in precipitation-1978-83.  
(Based on data from the National Atmospheric Deposition Program and the National Trends Network.)

Figure 2.30 The percentage trend in the volume-adjusted concentrations of sulfate in precipitation between 1978 and 1983

[Source: Pickering and Kapinos, 1985]

at two stations. Downtrends in  $\text{SO}_4^{=}$  and  $\text{NO}_3^-$  were poorly reflected by trends in pH.

In summary, available data are reliable, for the most part, only since about 1980. Few rigorous analyses have yet been conducted; however, some recent results that are available suggest a decrease in  $\text{SO}_4^{=}$  and deposition in eastern North America over the past five years. To date, thorough analyses (e.g. meteorological) have not been conducted to establish the cause of these changes. Sulfur emissions are known to have decreased during this period.

## 2.4.2 Visibility and Sulfate Aerosol\*

### 2.4.2.1. Introduction

Visibility is defined as the prevailing horizontal distance throughout at least half of the horizon circle at which it is just possible to distinguish with the unaided eye:

- a) prominent dark objects against the sky in daytime
- b) unfocussed moderately intense light sources at night.

Visibility deterioration is attributable to attenuation by gases and suspended aerosol particles in the atmosphere by absorption and scattering.

The daytime visual range,  $V$ , is more rigorously defined as the distance at which the apparent contrast,  $C$ , between a specific target and its background becomes just equal to the threshold contrast,  $C_t$ , of an observer. It is a function of the atmospheric extinction coefficient,  $b_{ext}$ ; the albedo, the visual angle of the target and the observer's threshold contrast:

$$V = \frac{1}{b_{ext}} \ln \frac{C}{C_t}$$

In the special case where the target is black,  $C=1$ , and the threshold contrast,  $C_t$ , is assigned a constant value equal to 0.02, the standard visibility,  $V'$  or meteorological range is

$$V' = \frac{1}{b_{ext}} \ln (0.2)^{-1} = K \frac{1}{b_{ext}}$$

where  $K$  is the Koschmieder constant and  $V'$  is inversely proportional to the extinction coefficient  $b_{ext}$ .

The extinction coefficient,  $b_{ext}$  is the sum of the medium's absorption and scattering coefficients, each computed as a weighted average over all wave-lengths in the visible spectrum,  $b_{ext}=b_s+b_a$  where  $b_s$  comprises three components: Rayleigh scattering by air molecules ( $\sim 0.12 \times 10^{-4} m^{-1}$  at sea level, Penndorf, 1957), scattering by aerosols without associated liquid water and that due to liquid phase water associated with hygroscopic aerosol constituents. The Rayleigh scattering is inconsequential,  $b_{ext}$  ranging in value from  $10^{-2} m^{-1}$  with very low visibility to  $10^{-4}$  in very clear air, and absorption accounting for less

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\*Prepared by A.D. Christie and L.A. Barrie



than 30% of net attenuation. (Lindberg and Laude, 1974). Early studies demonstrated that both light scattering and atmospheric aerosol volume concentrations are dominated by particles between 0.1 and 1.0  $\mu\text{m}$  diameter (Whitby et al. 1972) suggesting a correlation between the visibility and the fine particle fraction ( $< 2 \mu\text{m}$  diameter) of atmospheric aerosols. The relationship was confirmed by Horvath and Noll (1969). Using measurements with an integrating nephelometer and prevailing visibility as determined by two independent observers, they found for relative humidities less than 65%, a correlation of  $\sim 0.9$ . These results were confirmed in extensive tests of Charlson, 1969.

It has therefore been advocated that visibility records might serve as a surrogate for atmospheric boundary layer loading of species associated with acidification of surface waters.

Appel et al (1985) have carried out the most exhaustive study to date of the relative contributions to visibility reduction of both light scattering and absorption by specific pollutant particles and gases, under various sub and supersaturated environments, measuring sulfate and nitrate with minimum sampling artifacts. Using multiple regression methods, they derived a formula for the total extinction attributable to both fine and coarse particle fractions, to aerosols without associated liquid water and for liquid phase water associated with hygroscopic aerosol constituents, the latter being predominantly linked to the fine particle fraction of sulfate and nitrate aerosols. The relative humidity was one major factor whose inclusion in the multi-parameter regression resulted in a much improved aerosol pollutant to visibility correlation (from  $r=0.52$  to  $r=0.985$ ). Accordingly it was considered appropriate, in consideration of the visual range data base, where humidity was not well specified, that less scatter could be assured by elimination of all cases where the humidity exceeded a threshold above which it became significant.

#### 2.4.2.2 Data Availability

The nature and problems of the US visibility data base have been discussed by Reiss and Eversole (1978) and Vinzani and Lamb (1985). Data for Canada have been accumulated in the Atmospheric Environment Service climatic archives from in excess of 250 aviation reporting stations across the country. The variation in degree of exposure to increasing urbanization or local pollution, changes in observers, and in selected local "Markers" contribute to potential for change in the estimated prevailing visibility over the years, urbanization leading to gradual deterioration while the other effects are more likely to be associated with step changes. Furthermore, the reported resolution is a function of the range within which the observation occurs, being in fractions of a mile up to 3 miles, 1 mile in the range 3-15 miles and even coarser about 15 miles. Moreover, the requirement to note visibility "obstruction to vision" causes, for cases with values less than 7 miles, resulted in an artifact barrier at that value.

These obstructions to vision may be attributed to precipitation, smoke,

fog etc. phenomena unrelated to the secondary pollutants we wish to document so prescreening of the data to remove such cases becomes necessary. Further since humidity (Horvath and Noll, 1969) and the illumination (solar zenith angle) have been shown to influence visibility (Husar et al. 1979) it has been found advisable to further arbitrarily restrict the data base to hours between 10-16 local time and relative humidity below 70%. In the case of stations reporting at only synoptic hours that severely limits the data sample.

These data irregularities impose constraints on the credibility of inferences concerning statistical results derived from them.

#### 2.4.2.3 Analysis Methods

Individual station records have been studied using standard statistics (means and variance), the percentage frequency flux methods (Holzworth and Maga, 1960; Miller et al. 1972), the cumulative percentile method (Trijonis and Yuan, 1978, Sloane, 1982) and ridit analysis (Craig and Faulkenberry 1979). Attempts to study objectively regional patterns in visibility (or sulfate surrogate) are frustrated by the data base limitations noted earlier (Husar et al. 1979). While average local visibilities (or  $b_{ext}$ ) can be computed, local meteorological influences, aerosol sources and resuspension mechanisms combined with the heavy weighting of observations in the longer distance categories with their associated poor resolution are all factors that contribute to the high variability found in contiguous stations and the low confidence that can be placed on their absolute values.

The other methods, all based on relative frequency of occurrence of visibilities within selected ranges of values during successive intervals of sufficient duration to include a representative sample of observations, each give more reliable relative measures of local trend but their individual values can not be meaningfully aggregated into regional average values that would permit regional patterns to be quantitatively isoplethed for successive time periods.

#### 2.4.2.4 Studies with Canadian Data

Early studies in Canada were based on the computation of a "haze index" for various subsets of the meteorological reporting stations of the Atmospheric Environment Service chosen as representative of different regions (Munn, 1973; Inhaber, 1976; Vickers and Munn, 1977). The haze index was defined as the frequency of occurrence of prevailing visibilities in the range of 1 to 10 miles recorded over a climatic interval (season or year) of constant duration. The approach is therefore not strictly analogous to any of the percentage frequency of occurrence methods noted above since the total sample number at each location and successive period varies with specific 'obstructions to vision' and ambient moisture levels when the cases of relative humidity in excess of 70% were excluded to elevate the correlation with the sulfate aerosol.

Despite the method's shortcomings an attempt was made to extend the analysis to the approximately 250 observing stations representative of rural as well as suburban locations near major cities. It further showed the imprecision and local variability of the index as an indicator of background changes representative of the acid deposition scales.

A study was carried out on a selected subset of 91 stations having at least 15 years of observations representative of rural areas. The sample included the hours 1100 to 1400 local time with no recorded 'obstruction to vision' and with relative humidity less than 90%. The records for the period 1954-1979 were analysed by season (winter - 1st quarter, spring - 2nd quarter etc.). Statistics analysed were mean seasonal extinction coefficient and ridity. The ranges selected for the ridity classes were 0 to 9.6 km (0-6 mi.), 9.6 to 24 km (6-15 mi.) and > 24 km (> 15 mi.), the ranges being chosen to ensure the adequacy of sample size in each range. While the top range contains about 2/3 of the total population the observational resolution does not permit its subdivision though the mid-range (9.6 to 24 km) could perhaps benefit the ridity analysis if further sectioned into two (say 9.6 to 16 and 16 to 24 km).

The unreliability of means and variances computed from data samples such as visibility where the upper class is open (i.e. > 15 mi.) is well known and the variability in calculated values of mean extinction coefficient were not unexpected. Stations within similar regions showed little coherence and local changes generally were manifest by step changes, more likely associated with an observational artifact than a regional trend.

The ridity method, on the other hand, which analyses the relative frequency of occurrence of observations in ranked categories in specific time intervals in relation to those in a 'reference distribution' of long duration. The mean ridity can be interpreted as the probability that an observation from the selected sub-interval will be greater than that from the longer reference distribution.

$$\text{The mean ridity } R_t = \sum_{i=1}^k r_i \left( \frac{n_{it}}{n_t} \right) \text{ and } r_i = \sum_{j=1}^{i-1} P_j + \frac{1}{2} P_i$$

where

$$P_i = \frac{n_i T}{n_T}$$

$n_i$  represents the number of occurrences in category  $i < k$   
 $n$  represents the total occurrences in all categories and  
 subscripts  $t$  and  $T$  refer to the sub-interval (individual year)  
 and total observational set (25 years).

The mean ridity for the total period is  $0.5 \left( \sum_{i=1}^k P_i \right)^2 = 0.5$  and a mean ridity for any sub-interval below or above that value represents a displace-

ment of the probability density distribution of visibility to reduced or increased values respectively, relative to the local normal from the entire record.

Time series of station mean ridgets by year and season were plotted. Despite regional interstation variability an analysis of ridgets for the final five years of records used (1975-79) illustrated extensive regions in all seasons demonstrating improved visibilities as shown by ridgets above 0.5. The area of improvement is illustrated by Figure 2.31 where areas of ridgets above and below the reference period are shown as hatched and unshaded respectively.

With current visibility record quality it is not considered likely that regional scale trends can be interpreted in terms of trends in atmospheric sulfate unequivocally.

### Conclusions

The Canadian visibility data base is inadequate to delineate unambiguously inter-annual changes in atmospheric sulfate using visibility-derived average extinction coefficients as proposed by Husar et al., (1979) for the reasons stated in sections 2.4.2.2 to 2.4.2.4. We would further suggest that the degree of subjectivity involved in producing such maps for the Eastern U.S. from the data base shown in the paper by Husar et al. (1979) does not inspire confidence in that analysis.

The analysis of visibility can provide a useful indication of local relative trends in sulfate through the use of statistical analysis methods (ridit and cumulative percentile approaches) that minimize the problems due to observational methodology and quality (Northeastern U.S., Trijonis and Yuan; Mideastern U.S., Sloane, 1982; Western and Southwestern U.S., Vinzoni and Lamb, 1985; Québec and Southwestern Ontario, Leduc and Lamothe, 1985; 21 Canadian stations; unpublished time series of annual ridit by season, Christie, AES).

The open ended nature of the visibility category 'greater than 15 miles' results in heavy relative weight being assigned to that class in ridit analysis and limits the ridit accuracy but the introduction of more categories in the lower visibility ranges could improve the parameter precision (Leduc and Lamothe, 1985). The lack of inter-station coherence within regions suggests that local effects frequently dominate the regional scale picture particularly near centres of concentrated population density.

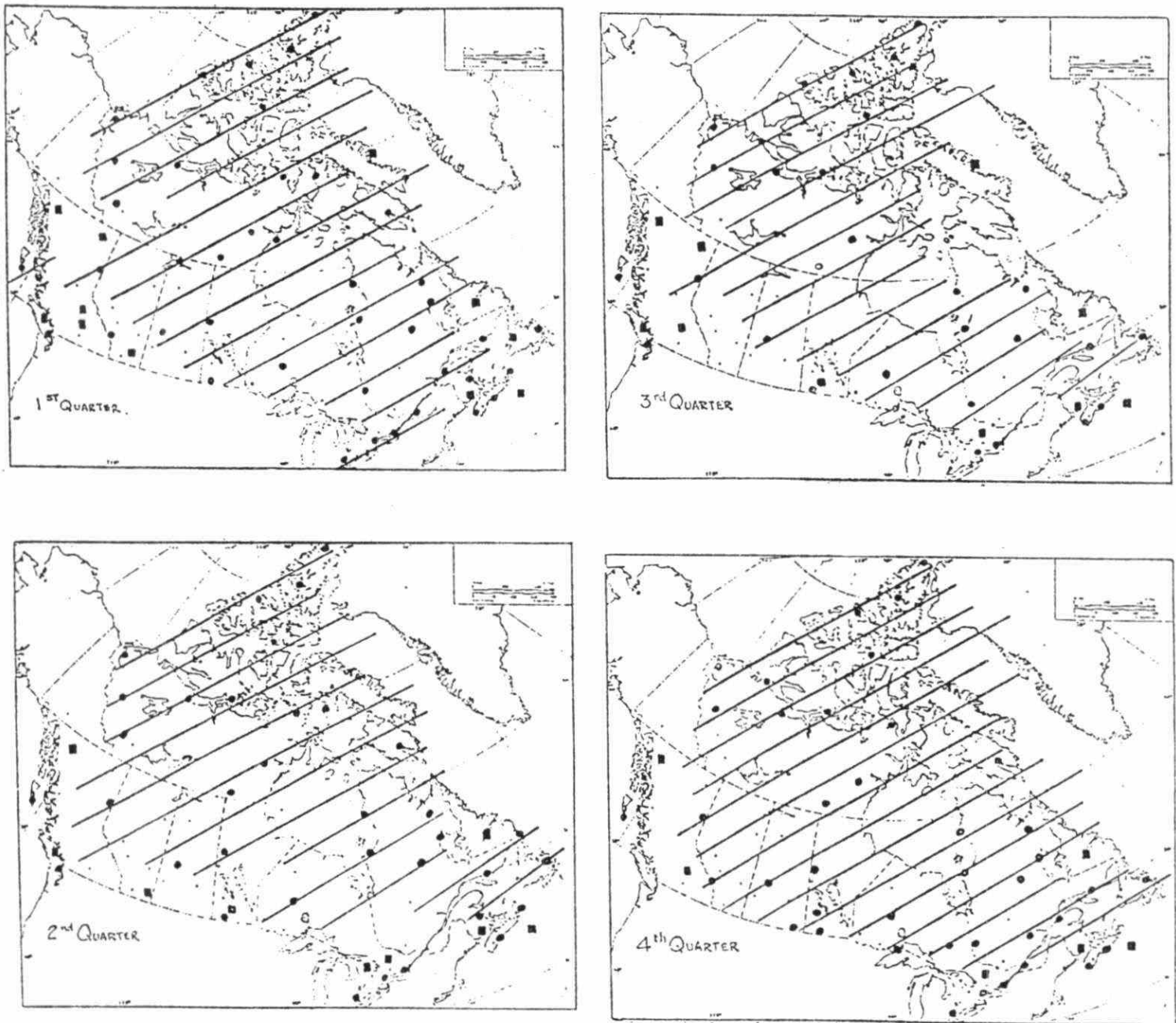


Figure 2.31 Regions within Canada, in each quarter, for which the mean ridits for the five year period 1975-79 are greater than 0.5 based on a reference distribution from 1955-79 are shown by the hatched areas. Those areas demonstrate that most of Canada with the exceptions of British Columbia, Southern Ontario and the maritime provinces showed generally improved visibility in the latter half of the seventies.



## 2.5. SOURCE-RECEPTOR RELATIONSHIPS FROM OBSERVATIONS

2.5.1 Pattern Association\*

The simplest method to link deposition with emissions is by association. From several recent studies of global budgets for sulfur the apportionment of anthropogenic emissions by geographical regions can be estimated as shown are in Table 2.8. Over 80% of the emissions are concentrated into the industrialized regions of the Northern Hemisphere with the remainder spread out over the rest of the world.

Table 2.8 The estimated percentage contribution to the global anthropogenic emissions of SO<sub>2</sub> by geographical region.

Region	% Contribution
China and Japan	24
USA and Canada	23
Eastern Europe & USSR	21
Western Europe (incl UK)	14
Remainder of N. Hemisphere	12
S. Hemisphere	6

Data collected by the Background Air Pollution Monitoring Network (BAPMoN) operated by the World Meteorological Organization show two large contiguous regions of heavy SO<sub>4</sub><sup>=</sup> wet deposition and low pH (< 5) over eastern North America and over Europe (Georgii, 1982, Whelpdale, 1984). Low pH values also occur over Japan (Whelpdale, 1984) but the full extent of the deposition patterns in the orient are not known due to a paucity of monitoring sites. However, in the Northern Hemisphere the heaviest deposition occurs over and immediately downwind of the major source regions clearly showing the strong geographical relationship.

Barrie et al. (1985) report historical snowcap acidity records in the Canadian high Arctic during this century that parallel the emissions of acidic gases (SO<sub>2</sub> and NO<sub>x</sub>) in Eurasia (the source of Arctic air pollution). This is observational evidence that clearly links acidic emissions and deposition on a scale of 10000's of Km. Concentrations in snow increased by 75% between 1956 and 1978 as SO<sub>2</sub> emissions doubled.

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\*Prepared by P.W. Summers

In eastern North America these geographical associations can be seen in more detail from maps of the emissions by states or grid squares and the concentration/deposition patterns, such as shown by Barrie and Hales (1984). The centroid of the high emission zone for  $\text{NO}_x$  south of the Great Lakes is somewhat further north than for  $\text{SO}_2$  due to the larger contribution from urban areas. This is reflected in the slight shift northward of the  $\text{NO}_3^-$  deposition pattern compared to  $\text{SO}_4^{2-}$ . Ammonia emissions are a maximum in the high plains of the U.S. due to the large amount of agricultural activity including livestock feed lots, and is reflected in the maximum concentration/deposition of ammonium in the same area with a "plume" extending downwind across the Great Lakes.

Finally, the suggestions that a substantial fraction the  $\text{SO}_4^{2-}$  deposition in eastern North America may be due to natural sources have been negated by Galloway et al. (1984). Using data from the Global Research Network referred to in section 2.3.1, Galloway used the average background values of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  to calculate an enrichment factor for the concentrations and produced the maps shown in Figures 2.32. These clearly show the maximum enrichment over and immediately downwind of the major source regions by a factor  $>16$  for  $\text{SO}_4^{2-}$  and  $>10$  for  $\text{NO}_3^-$ .

These associations are obviously subjective but can be made successively more quantitative by a variety of increasingly sophisticated analysis techniques ending in the ultimate goal of numerical simulations as described in the following sections.

#### 2.5.2 Budget Studies\*

Atmospheric pollutant budgets provide a useful means of evaluating the state of knowledge about pollutant inflows and outflows for a region. MOI Report No. 2F-I (MOI, 1982) summarized results of regional budget studies in North America up to about 1980, and identified their uses and limitations. Several subsequent investigations which have sought to refine these early estimates are reviewed briefly below and summarized in Tables 2.9 and 2.10.

Olson et al., (1982) constructed sulfur budgets for Ontario, Quebec and the Atlantic Provinces on the basis of 1978 meteorological data and  $\text{SO}_2$  emissions from the 1970-1974 period, using the AES LRTAP model. For eastern Canada the annual S transboundary input was 2 Tg; emissions were 1.8Tg; total deposition was 2.4 Tg and outflow was 1.4 Tg. The computational approach allowed transborder flows to be determined along border segments, between provinces, and between Canada and the USA. Overall uncertainty in the budget was estimated at 40-50%.

Johnson (1983) reviewed types and applications of regional-scale LRT

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\*Prepared by D.M. Whelpdale and M.P. Olson

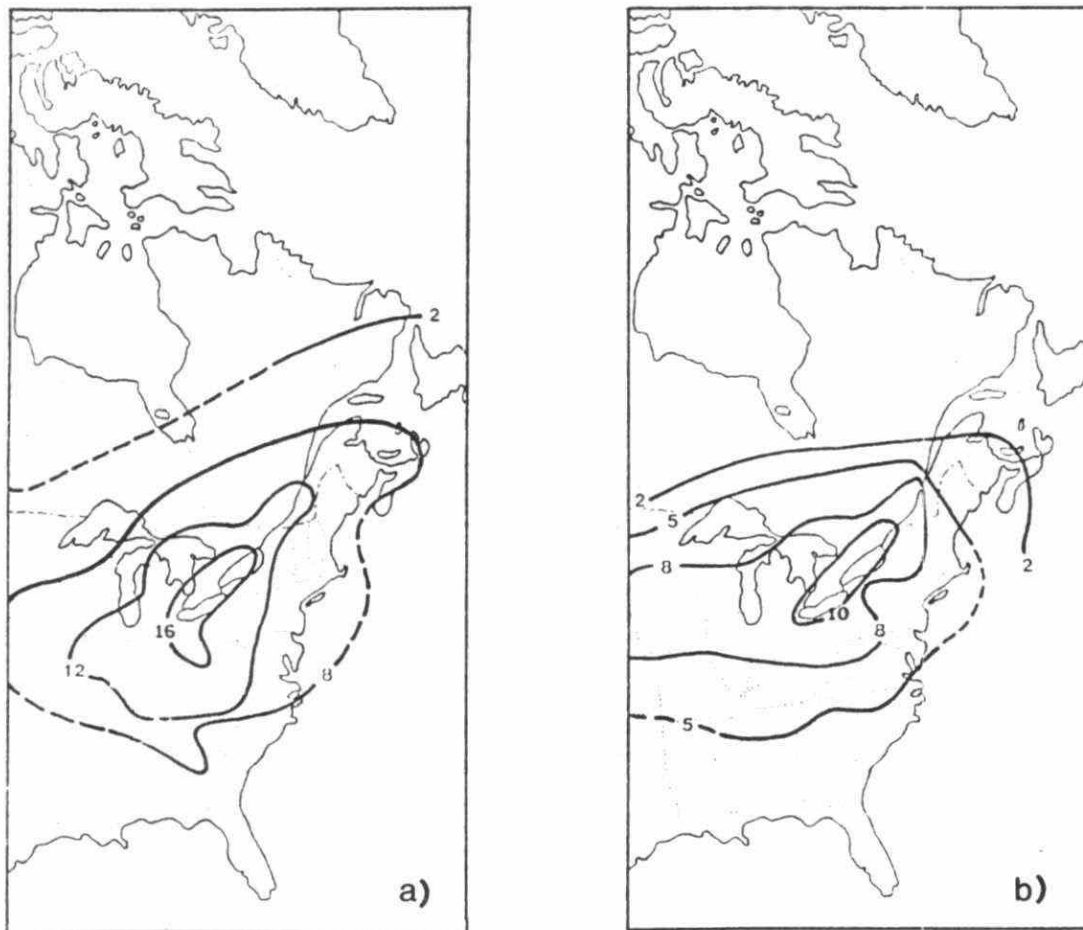


Figure 2.32 The enrichment factor in North America precipitation relative to remote areas: a) for sulfates b) for nitrates

[Source: Galloway et al., 1984]



Table 2-9: A Comparison of Recent Sulfur Budgets (TgSy<sup>-1</sup>)

Source	Galloway & Whelpdale (1980)	Olson et al. (1982)	Johnson (1983)	Johnson (1983)	Bischoff et al. (1984)	Galloway et al. (1984)	Voldner & Shannon (1984)	Shannon & Lesht (1985)	Fay et al. (1985)
Method	Data anal.	AES model	(2) ENAMAP MODEL	(3) ASTRAP model	data anal.	data anal.	AES model	ASTRAP model	Fay model
Year	late 1970's	1980	1977	1975	1970's	1980	1981	1984	1980-82
<u>Emissions</u>									
e Canada (man)	2.1	1.8	1.9	2.1				2.2	2.4
(nat.)	0.3								2.0
e U.S.A. (man)	14.0	14.0	14.1	11.9	11.4			12.9	12.6
(nat.)	0.4								10.2
e NA (man)	16.1	15.8	16.0	14.0			11.7		15.0
(nat.)	0.8						0.8		12.2
<u>Deposition</u>									
eUS sources to eUS			10.7	5.4				6.1	3.7
eUS sources to eCan		1.1	0.7	1.2			1.3	1.0	2.5
eCan sources to eUS			0.4	0.2				0.3	0.2
eCan sources to eCan	1.3	1.2	0.9			0.6	1.0	1.0	
Total to eUS	5.8		11.1	5.6	5.1			6.4	4.0
Total to eCan	4.2	2.4	1.9	2.2			1.9	2.0	3.4
Total to eNA	10.0		13.0	7.8		7.9		8.4	7.4
<u>Inflow from West</u>	0.5						0.5		
<u>Outflow to East</u>	4.3				3.0	4.3			
<u>Cross Border Flow</u>									
eUS to eCan	2.0	2.0 <sup>(1)</sup>			3.3				3.4
eCan to eUS	0.7	1.2							0.4

(1) Total cross-border flux including mass returning to country of origin

(2) Maritime Provinces not included

(3) Derived from one summer and one winter month

(4) Numbers are for all of Canada and all of U.S.A.

Table 2.10: A Comparison of Available Nitrogen Budget Figures ( $\text{TgNy}^{-1}$ )

Source	Logan (1983)	Bischoff <u>et al.</u> (1984)	Galloway <u>et al.</u> (1984)	Shannon & Lecht(1) (1985)
<u>Method</u>	data anal.	data anal.	data anal.	ASTRAP model
<u>Year</u>	~1980	1970's	~1980	1984
<u>Emissions</u>				
eCan (man)	0.5			0.6
eUSA (man)	3.7	3.9		6.1
eNA (man)	4.2			6.7
<u>Deposition</u>				
eUS to eUS				3.0
eUS to eCan				0.4
eCan to eUS				0.1
eCan to eCan				0.2
Total to US	1.5-2.6	1.0		3.1
Total to Can	0.6-1.0			0.6
Total to NA	2.0-3.6			3.8
<u>Inflow from West</u>	0.3			
<u>Outflow to East</u>	0-3.7	1.6	1.1-3.2.	
<u>Cross Border</u>				
eUS to eCan		1.3		
eCan to eUS				

(1) Numbers are for all of Canada  
and all of U.S.A.

models. One example of model intercomparison described large-scale sulfur exchanges and sheds some light on regional-scale budgets for southeastern Canada and the eastern U.S. An important point made by Johnson is that when comparing results from different approaches to a problem (modelling large-scale fluxes, in this case), it is essential that the basic inputs are the same - e.g. geographical area, emissions and meteorological data, time period, etc. Where possible, these differences are identified in the Tables.

Logan (1983) published a detailed review of the cycle of nitrogen oxides in the troposphere from both global and North American regional perspectives. The quality and quantity of data available for the oxides of nitrogen are generally less than for sulfur, and thus estimates of large-scale nitrogen fluxes are correspondingly less reliable. Nevertheless, Logan's values (Table 2.10) provide a useful first estimate for future studies. When possible, uncertainty estimates and ranges are given.

Bischoff et al., (1984) constructed a geochemical mass balance model for  $H^+$ ,  $NO_3^-$  and  $SO_4^{2-}$  for the eastern United States in order to investigate the pathways and fluxes of these substances throughout the geochemical system in this region. Their results applicable to the atmosphere are given in Tables 2.9 and 2.10. The authors emphasize the utility of such regional mass balance modelling for organizing and compiling information, identifying critical processes, and quantifying source and sink fluxes.

Galloway et al., (1984), in refining estimates for the flux of sulfur and nitrogen eastward from North America, updated their earlier S budget for eastern North America (Galloway and Whelpdale, 1980 - also given in Table 2.9 for comparison) and suggested revisions to Logan's (1983) numbers. More recent emissions and wet deposition information lead to an improved balance for the regional sulfur budget. However, a comparison of the expected relative behaviour (transformation chemistry and removal processes) of sulfur and nitrogen suggests that the calculated N leaving North America is too large, and, thus, that more is being deposited than current estimates suggest (see Tables 2.9 and 2.10).

Voldner and Shannon (1984) have compared predicted and observed sulfur deposition fields for eastern Canada using the ASTRAP model. The more recent input data used included: analyzed wind and precipitation fields for 1980 and 1981, and 1978 (US) and 1980 (Canada) sulfur emissions. Their estimates for 1980 and 1981 gave similar results. Predicted results showed excellent agreement with quantities derived from observations, thus giving confidence to the budget estimates derived.

Shannon and Lesht (1985) have used the ASTRAP model to calculate large-scale fluxes of nitrogen oxides in North America, and in particular between the US and Canada. The model assumes linearity between emissions and deposition, and uses the same parameterization methods, but with different rates, as in the computations for sulfur. Shannon and Lecht

find that the transport distance scale for deposition of  $\text{NO}_x$  appears to be shorter than that for  $\text{SO}_x$ . For comparison, recent S flux computations are also given (see Tables 2.9 and 2.10).

Fay et al., (1985) have recently applied their analytical LRT model to the question of source apportionment of wet sulfate deposition in eastern North American. As a by-product of their analysis, North American transboundary fluxes are obtained. They find a US to Canada flux of  $3.4 \text{ Tg Sy}^{-1}$ , somewhat larger than most other estimates, and a return flux of  $0.4 \text{ Tg Sy}^{-1}$ . These estimates were not made in the context of a budget, but are shown in Table 2.9 for comparison.

Table 2.9, which summarizes the estimates made for the various budget terms, provides a useful indication of some of the sources of variability in the calculation (e.g. different approaches, models, base years, emissions and geographical regions), and of the resulting uncertainties in the results (differences in the computed values). Two important points of methodology must be noted:

- (1) Only two of the studies cited included natural emissions, and were thus considering total (anthropogenic plus natural) fluxes.
- (2) A distinction must be made between "total" and "net" transboundary flux. The models are able to attribute deposition to source regions (first four rows under the heading "Deposition"), whereas the data analysis studies only estimate total transboundary flux (last two rows in Table 2.9). The difference is the material which passes directly through the atmosphere of a neighboring country without being deposited.

From the perspective of this section where emphasis is on source-receptor relationships, the importance results from Table 2.9 are further summarized in Table 2.11 in the form of simple  $2 \times 2$  source-receptor matrices for total deposition of S (wet + dry). An examination of the top row of the matrices reveals that estimates for the deposition of eastern Canadian emissions in eastern Canada range from 0.6 to 1.3, whereas the eastern US contribution to deposition in eastern Canada ranges from 0.7 to  $2.5 \text{ Tg Sy}^{-1}$ . The ratio of US to Canadian contributions in eastern Canada ranges from 0.6 to 2.5. An examination of the available transboundary flux numbers reveals that the ratio of northward to southward fluxes ranges from about 3 to 12. In summary, based on Table 2.11 and knowledge of the various methods used, it would appear that the US contribution to deposition in eastern Canada is about the same or slightly greater than the eastern Canadian contribution. It would also appear that US to Canada cross-border flux exceeds Canada to US cross-border flux by a factor of approximately 3 or 4.

As Table 2.10 shows, the art of estimating nitrogen oxide transboundary fluxes is at an early stage.

Table 2.11: Simple 2x2 Source-Receptor Matrices for Total Sulfur Deposition Based on Budget Studies ( $\text{TgSy}^{-1}$ )**A. Models**

Olson et al. (1982)

From To	eCan	eUS
eCan	1.3	1.1
eUS	-	-

Johnson (1983) - ENAMAP

From To	eCan	eUS
eCan	1.2	0.7
eUS	0.4	10.7

Johnson (1983) - ASTRAP

From To	eCan	eUS
eCan	0.9	1.2
eUS	0.2	5.4

Voldner &amp; Shannon (1983)

From To	eCan	eUS
eCan	0.6	1.3
eUS	-	-

Shannon &amp; Lesht (1985)

From To	eCan	eUS
eCan	1.0	1.0
eUS	0.3	6.1

Fay et al. (1985)

From To	eCan	eUS
eCan	1.0	2.5
eUS	0.2	3.7

**B. Data Analysis<sup>(2)</sup>**

Bischoff et al. (1985)

From To	eCan	eUS
eCan	-	3.3
eUS	-	5.1

Galloway &amp; Whelpdale (1980)

From To	eCan	eUS
eCan	-	2.0
eUS	0.7	-

(1) See footnotes to Table 2-9

(2) Values are for total cross boundary flows

### 2.5.3 Tracer Studies\*

The approaches in the preceding two sections show qualitative associations between deposition and emissions, but there is no way that from observations of  $\text{SO}_4^{=}$  deposition alone, the particular source of the  $\text{SO}_4^{=}$  can be distinguished from all the upwind precursor emissions. However, natural trace substances occurring in conjunction with emissions from particular sources (often referred to as "tracers of opportunity") offer the potential to establish source-receptor relationships. The general use of tracers, both natural and artificial, in atmospheric sciences is very thoroughly reviewed in a workshop report (Los Alamos National Laboratory, 1984).

#### 2.5.3.1 Tracers of Opportunity

Since 1982 there has been a great deal of discussion on the possibility of using the trace elemental composition of atmospheric aerosols as tracers of origin on a regional scale. The studies of Rahn and Lowenthal (1984, 1985) in eastern North America indicate that six aerosol trace constituents are useful indicators of pollution source region: arsenic (As), antimony (Sb), selenium (Se), anthropogenic vanadium (V) and manganese (Mn), zinc (Zn) and indium (In). It is claimed that with these elements one can differentiate particulate sources in North America into five source regions: New England, Central East Coast, Lower Mid-West, Upper Mid-West and Southern Ontario. Based on 4 to 12 samples in each source region with the exception of the Upper Mid-West for which 48 were available, it is shown that each of these regions have aerosols of a distinctly different composition. The weakness in this is that so few measurements in the source regions have been made. However, if one assumes that the source 'signatures' proposed are indeed representative and if one makes an additional assumption that these signatures do not change much as a result of selective removal, one can then use these signatures to analyze what fraction of a particular tracer element in a 24 hour average sample taken several hundred to a thousand kilometers downwind of these sources originates from each source. The second assumption is somewhat justified because the elements chosen are mainly concentrated in fine-particle aerosols less than 2 micrometers in diameter that are not removed rapidly from the atmosphere. An application of such a method to measurements in Vermont and Rhode Island, indicates that, on average, the Northeast is the most important source of aerosol elements that are broadly distributed over eastern North America or enriched in northeastern emissions (i.e. V, Sb, Zn, Mn). On the other hand, for elements enriched in distant sources, such as As and In from Canadian smelters and Se and S from the Mid-West, the contributions of the distant sources may equal or exceed those from the Northeast. This conclusion is interesting because it essentially agrees with the predictions of long range transport models used in the MOI to assess source-receptor relationships. Thus, with regard to previous

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\*Prepared by P.W. Summers and L.A. Barrie

controversy surrounding the aerosol signature issue, one can say 'Much ado about nothing'. A major weakness of the approach is that it cannot be used to quantitatively apportion sources to substances in aerosols that have gaseous precursors (i.e.  $\text{SO}_4^{2-}$ ).

Another attempt to use aerosol composition to shed light on pollutant source regions has been made recently by Pacyna (1985) in Europe. Analyzing aerosol composition as a function of wind sector in Scandinavia, he concluded that the elements chromium (Cr), copper (Cu), arsenic (As), selenium (Se), molybdenum (Mo), tin (Sn) and vanadium (V) were useful in distinguishing eastern and western European primary particulate pollution but not so useful in identifying sources of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ .

There is little doubt that the gaseous and particulate composition of atmospheric pollution contains valuable information that can be used to improve our understanding of pollutant origin. There is a need to experimentally test the assumptions made in current approaches.

#### 2.5.3.2 Artificial Tracers

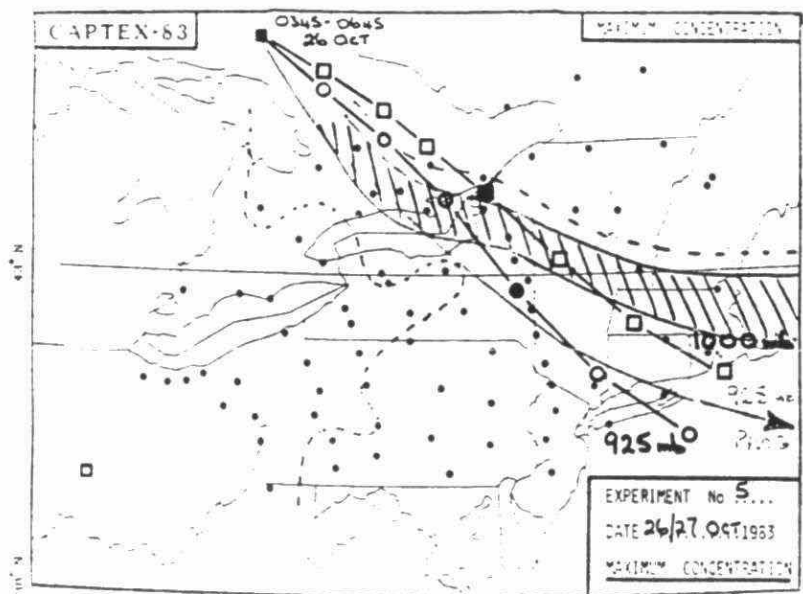
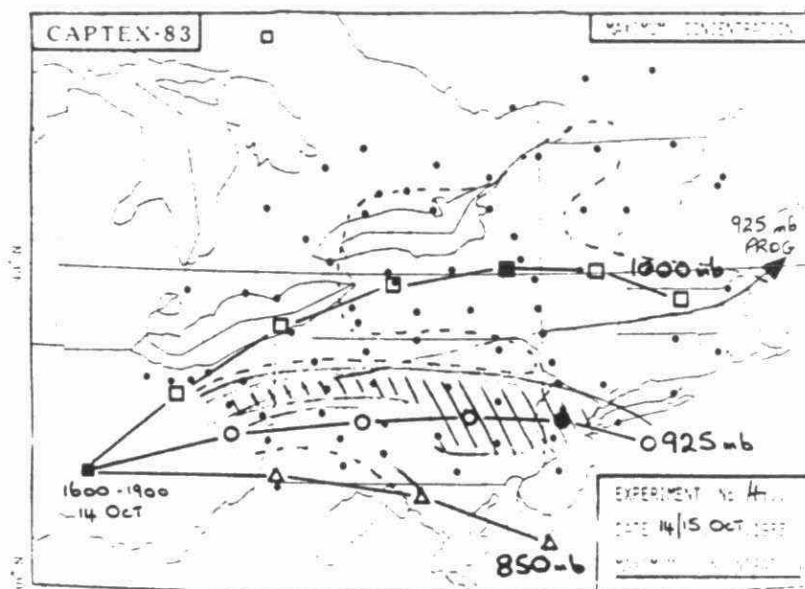
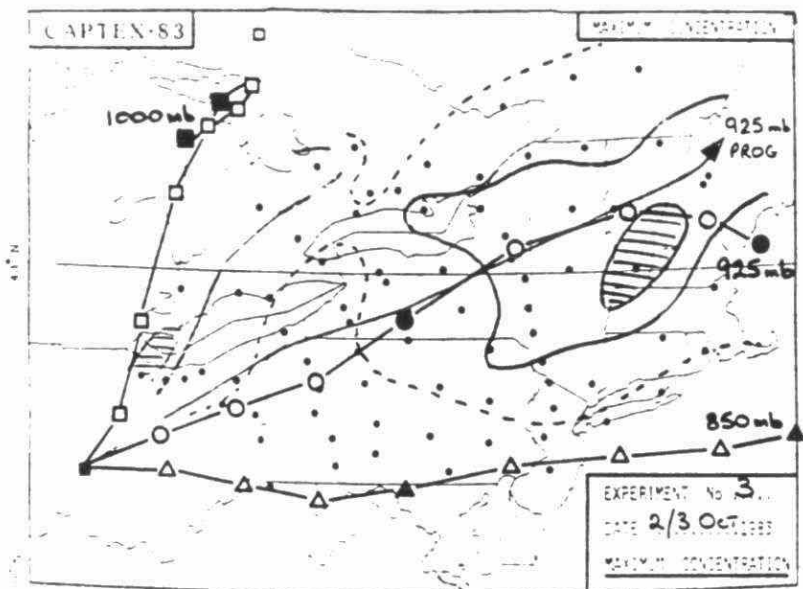
As far as acid rain and long-range transport issues are concerned the major new development has been the successful CAPTEX-83 carried out over the N.E. United States and S.E. Canada in September-October 1983. A full description of the experiment and a review of the operational logistics were presented by Ferber (1985).

A comparison between the air trajectories generated by the AES-LRTAP model and the observed ground-level tracer measurements has been made by Summers and Olson (1986). Under the simple meteorological situations represented by the CAPTEX-83 ground-level tracer releases, the following main results were found:

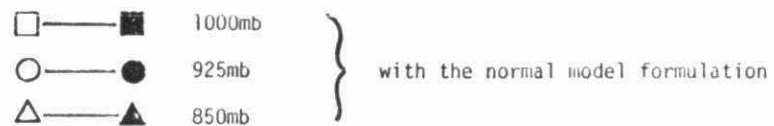
- a) In the four warm air advection cases (Dayton releases) the trajectories showed strong speed and directional wind shear in the lowest 300mb of the atmosphere. The ground-level tracer concentration pattern showed substantial cross-wind spread with the northern edge delineated by the 1000mb flow and the southern edge by the 850mb flow.
- b) In the two cold air advection cases (Sudbury releases) the trajectories showed small directional shear in the lower atmosphere and the tracer was confined into a narrow plume.
- c) The path followed by the maximum ground-level concentrations was best represented by the 925mb trajectory, with the speed of motion agreeing well for the first 18-24 hours (For example see Figure 2.33).
- d) The forecast trajectories prepared 36 hours before the release were almost as good as the post-factor diagnostic trajectories in simulating the trace motion.



Figure 2.33 Examples of the observed tracer concentrations and the modelled air trajectories for three of the CAPTEX-83 experiments



Maps showing the maximum tracer concentration field for all seven experiments. Superimposed on these fields are the various computed model trajectories according to the code indicated below. Positions are shown every 6 hours with the heavier dots etc. indicating the 24 hr positions.





- e) One dramatic case of flow de-coupling was observed in which one portion of the tracer moved NE from Dayton into SW Ontario whilst the other portion moved ENE aloft and surfaced in high concentration over New England 36 hours later (See Figure 2.33).

It thus appears that under the simple meteorological regimes represented by the CAPTEX-83 experiments (i.e. no precipitation or frontal passages) the AES-LRTAP model performed well in representing the direction and speed of motion of the main bulk of the tracer, at least for the first 24 hours after release. How well these results can be extrapolated to other more complex situations is not known and can only be determined by further experiments. However, these results are encouraging and do not negate the use of the simple model as a qualitative tool in the development of acid deposition control strategies.

A workshop was held at the Argonne National Laboratory, Illinois in November 1985. The tracer concentrations and patterns predicted by four trajectory models (including the Ontario Ministry of the Environment "LRTAP" model) were compared with the observed tracer concentrations in a "blind" test. Some models predicted peak concentrations well and others the tracer spread well. In two of the experiments, the observed double tracer peak was correctly predicted by two of the models. All models simulated the tracer motion reasonably well, but none could be selected, at this stage, as being the best overall.

During 1984, Canadian scientists participated in two U.S. studies of the feasibility of using field data and experiments, including the extensive use of tracers, to empirically estimate source-receptor relationships as an alternative to using numerical models. Both of these projects MATEX (Massive Aerometric Tracer Experiment) and COMPEX (Comprehensive Atmospheric Experiment) were put on hold for several reasons including:

- a) the high cost, of the order of \$100 million.
- b) the political unacceptability of using radioactive sulfur isotopes as tracers and the limitations imposed on the experimental design by using only inert tracers.
- c) the propagation of errors within a scheme to empirically determine loss terms along source-receptor pathways.
- d) the number of untested assumptions or experimental approaches that would have to be used.

A series of pre-MATEX experiments were proposed to resolve the problems but as yet none have been funded.

The use of artificial tracers to study LRT is a new technology and the full potential has yet to be realized but establishing the relative merits of the experimental approach versus numerical modelling simulations is not easy. They are, in fact, complementary and both will no doubt continue to be used.

#### 2.5.4. Trajectory Analyses and Other Meteorological Studies\*

An analysis of long-term trends in emissions and deposition in Europe and North America has been complicated by both uncertainty in historical emission rates, and lack of suitable long-term deposition data (National Academy of Sciences, 1983; Hidy et. al., 1984; Likens et al., 1984; Granat, 1978; Rodhe and Granat, 1984). Although substantial changes in regional SO<sub>2</sub> emissions have taken place during the past 20-30 years (the period when any deposition data of acceptable quality have been collected) on both continents, corresponding changes in sulfur deposition are not definitive. The early work of Granat (1978) with European precipitation chemistry data, for example, indicated that the increase in emissions during the fifties and sixties did not seem to be reflected in an increase in the average deposition rates. However, a subsequent analysis by Rodhe and Granat (1984) suggested a reasonable correspondence between emissions and deposition. Precipitation sulfate concentrations observed at most of the Scandinavian stations, for example, were generally consistent with the estimated emission changes in several of the countries known to contribute significantly to deposition in Scandinavia. In North America, the most extensive historical data set - that from the Hubbard Brook network in New Hampshire - appears to demonstrate a decline in sulfate concentrations similar to the general regional reduction in SO<sub>2</sub> emissions (National Academy of Sciences, 1983; Likens et al., 1984). However, as Hidy, et. al. (1984) have pointed out in their extensive discussion on North American trends in historical acid precursor emissions and their airborne precipitation products, whereas changes in precipitation sulfate at rural sites in Central New York State and New Hampshire reflect SO<sub>2</sub> emission changes (nearby source regions dominating more distant sources), other sites in western New York and north central Pennsylvania show no proportionality between emissions and precipitation sulfate during the same period.

The interpretation of long-term trends at a given monitoring site is difficult for a number of reasons (apart from potential errors in the emission estimates and deposition measurements, due to such factors as contamination by dryfall, for example), not least among them the fact that deposition at most receptor areas of concern is the resultant of small contributions from many sources extending over a large area, and the very large inherent variability in precipitation chemistry. The importance of this latter factor in assessing the effects of emission controls has been discussed by Hidy (1984), who presents evidence illustrating that repeated observations over many years may be required to see even modest changes in precipitation chemistry. Wet deposition trend analysis has been also considered by Munn et al. (1984). In spite of intensive current efforts to improve our analytical tools for atmospheric deposition trend analysis, it is unlikely that definite conclusions on source-receptor relationships, resulting from analysis of long-term trends of emissions and deposition in North America, will be possible for a number of years to come, mainly because the necessary air and precipitation chemistry database has not yet been accumulated.

An alternative approach is to examine past occasions when emission reductions have occurred at specific sources, resulting from plant shutdowns or the imposition

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\*Prepared by M.A. Lusi W.H. Chan, K.G. Anlauf, L.A. Barrie, P.W. Summers and M. Ferland.

of controls. Trajectory analysis, applied to the interpretation of observations from regional air and precipitation monitoring sites, has been a useful tool in examining source-receptor relationships on such occasions. There has recently been an extensive review of this subject by Hidy (1984), with further discussions by Coffey, Summers, Wolff, Durham, Foley, McKee, Altwicker, and Hidy (1984). These authors agreed that some qualitative source-receptor relationships could be drawn from wind or air mass trajectory sector analyses of ambient air and precipitation chemistry data. However, one should bear in mind the potential uncertainties due to the influence of local sources, changes in emission characteristics (e.g. stack heights), complications due to frontal passages, and so on.

The main purpose of this section is to summarize the results of some of the more recent work, using trajectory and other meteorological analyses, which has examined changes in regional deposition measurements due to emission changes. The discussion will primarily be concerned with past observations (-on the meso- or larger scales) of changes in deposition due to emission reductions at specific sources, with two questions in mind, namely (i) were there any observable changes in the wet and dry deposition rates when the emissions were altered? and (ii) did the observations cast any light on the question of linearity, i.e., did a change in emissions of x% at the source also cause a change of x% in the long-term deposition attributable to that source, at the receptor area of interest? Because of the very sparse information on nitrogen compounds, only sulfur oxides will be considered.

A major study of relevance here has been carried out in Ontario, and has examined the effect on atmospheric deposition of the INCO and Falconbridge smelters at Sudbury during the late 1970's and early 1980's. At that time, these smelters emitted approximately one-half of the provincial total  $\text{SO}_2$  (Yap, 1984). The INCO smelter is one of the largest  $\text{SO}_2$  emission sources in North America, with a typical annual emission rate of 500-800 thousand tonnes (emanating from a 381 m "superstack"). Falconbridge emission rates are roughly one-fifth those of INCO.

An aerometric analysis of the extensive air and precipitation data set collected over several years in the Sudbury Basin (i.e., within approximately 40 km of the smelters) led to the conclusion that the larger of the two smelters, INCO, contributes only 8% and 25% respectively of the long-term wet and dry sulfur deposition to the Basin as a whole (Chan et al., 1984). Note that total annual wet and dry deposition rates in the Sudbury area are approximately 0.8 and 0.2 g S/m<sup>2</sup> respectively (Chan et al., 1985). A number of shutdowns of the Sudbury smelters have provided an opportunity for assessing the impact of such sources farther afield as well. Scheider et al. (1981) discuss the results of bulk deposition measurements in the Sudbury Basin, and the ecologically sensitive Muskoka-Haliburton area, about 200 km southeast of Sudbury, during a prolonged shutdown of the INCO smelter in 1978 and 1979. Although there were definite decreases in the Sudbury-area bulk sulfate deposition measurements, no significant decreases in sulfate or hydrogen ion deposition could be detected at Muskoka - Haliburton. Summers (1984) found similar results at a number of CANSAP monitoring stations in eastern Canada. During a subsequent smelter shutdown in 1982 and 1983, Ontario Ministry of the Environment scientists carried out an extensive analysis (including trajectory analysis) of the air and precipitation data collected at a number of monitoring sites in the province, out to about 500 km from the source (Yap and

Kurtz, 1984; Tang et. al., 1984; Lusi, 1984). Quantification of the smelter impact on the wet sulfur deposition beyond the Sudbury Basin proved to be a very difficult task, even with detailed meteorological stratification of the data, due to the limited sample size and the relatively small smelter contribution to a large and "noisy" background signal. It was estimated that the smelter contributes less than about 15% of the total sulfur wet deposition at a number of sites in various compass directions from Sudbury (Lusi, 1984) i.e., less than about  $0.1 \text{ g S/m}^2\text{.y}$  at each site. The smelter contribution to the sulfur dry deposition was found to range from less than 4% of the total (i.e., less than  $0.005 \text{ g S/m}^2\text{.y}$ ) at a site 800 km to the northwest of Sudbury, to less than 20-50% of the total (amounting to less than  $0.2\text{--}0.3 \text{ g S/m}^2\text{.y}$ ) at various sites 200-400 km to the east and northeast of Sudbury (simple trajectory analysis favoured the lower percentage as an upper limit of the smelter contribution). These studies clearly illustrate the difficulties involved in attempting to extract the contribution of a particular source (albeit a large one) from the total sum of emission contributions over a large area, and, at the least, make it clear that the deposition problem will require widespread abatement measures to achieve target loadings.

The next study of relevance was carried out by the Tennessee Valley Authority (Parkhurst et. al., 1984), who examined the effect on regional  $\text{SO}_2$ , particulate sulfate, and precipitation sulfate measurements of a an approximately 50% reduction (during the period 1978-1983) in  $\text{SO}_2$  emission rates from TVA plants in Alabama, Kentucky and Tennessee (the 1983 emissions were approximately one million tons). The conclusions of Parkhurst et al. regarding the impact of TVA emission reductions on concentration levels of the secondary pollutants - particulate and precipitation sulfates - are similar to those of the Ontario Ministry of the Environment workers. They found no measurable change in either local or regional concentrations within the Tennessee Valley region over the five-year period, although meteorological analysis of daily measurements showed that TVA emissions do exert a significant influence on particulate and precipitation sulfates under specific transport/transformation conditions (Parkhurst et al. apparently did not attempt to quantify the overall effect of the TVA emissions on secondary pollutant levels, based on the frequency of occurrence of these special transport/transformation conditions). Parkhurst et al.'s results suggest that other sources within and outside the TVA region exert a very significant influence on Valley-wide secondary pollutant levels, while, by the same token, TVA sulfur sources influence other, downwind areas.

It is interesting to note, however, that TVA emission reductions resulted in an approximately proportional decline in both local and regional ambient  $\text{SO}_2$  levels, and hence,  $\text{SO}_2$  dry deposition. This is an important conclusion, since in the TVA region, dry deposition of sulfur is expected to be comparable to wet deposition.

The final set of investigations have considered variations in air and precipitation quality as a result of changes in  $\text{SO}_2$  emissions from a group of non-ferrous metal smelters in the southwestern United States near the U.S. - Mexican border (Eldred et al., 1983; Yuhnke and Oppenheimer, 1984; Oppenheimer et. al., 1985; Niemann, 1985), whose annual  $\text{SO}_2$  emissions have fluctuated between about 700 and 1200 thousand tonnes during the 1980-1983 period. Eldred et al. compared particulate sulfate levels, at monitoring stations within 700 km, during smelter shutdown and operating periods in 1979-1981, and found a marked smelter impact. They found



that the smelters contributed about 70% of the particulate sulfate at sites within about 100 km, and about 50% throughout the rest of the monitored region, but did not extend their analysis to establish a quantitative relationship between smelter emission rates and regional sulfate levels. Yuhnke and Oppenheimer (1984), and Oppenheimer et al. (1985), subsequently considered the smelter impact on downwind precipitation sulfate concentrations (out to about 1000 km), and found that, as with Eldred's particulate sulfur results, a large fraction of precipitation sulfate originates at the smelter sources. This was thought to be due to the strong dominance of the smelters over other emission sources in the area, and the persistence of winds from the smelters towards the monitors in the region of interest (such channelling between mountain ranges does not occur in the Sudbury or TVA areas discussed earlier). In fact, Oppenheimer et al. went on to conclude that there is a linear relationship between the smelter emissions and precipitation sulfate levels at remote intermountain sites, and, moreover, that their results imply that major nonlinearities are absent from the atmospheric chemistry of  $\text{SO}_2$  over extended areas of the United States. This rather controversial conclusion was quickly challenged (Niemann, 1985) on the grounds that the use of carefully screened precipitation data, and monthly or seasonal (rather than annual) emissions data, shows that the smelter emissions are not the predominant source of precipitation sulfates, nor is there a convincing case for linearity between emissions and regional deposition. Thus, the interpretation of this particular data set is still the subject of a lively debate (Machta, 1985).

To summarize: using past experiments of opportunity alone, we cannot predict with certainty what changes in concentration and deposition will result from given changes in emissions. Trajectory and other meteorological studies, carried out around strong emission sources in eastern North America (i.e., within about 500 km of Sudbury, and in the Tennessee Valley), have experienced difficulty in quantifying the impact on airborne and precipitation sulfates resulting from  $\text{SO}_2$  emission changes, let alone examining the linearity question. Changes in regional  $\text{SO}_2$  levels, and hence  $\text{SO}_2$  dry deposition, did, however, suggest a linear relationship to  $\text{SO}_2$  emissions in at least one (the TVA) study. Due to peculiar topographical and meteorological features, air and precipitation measurements of sulfates in the intermountain West showed a rather strong correlation with smelter emissions, but the question of linearity between emissions and deposition, and the relevance of the western observations to other areas of North America, is still the subject of debate. One fact does seem to be clear from these studies: achievement of target loadings in sensitive areas of eastern North America will require widespread abatement measures; in other words, control of local emission sources alone is unlikely to prove effective. This conclusion is consistent with current estimates of the residence time of  $\text{SO}_4$  and  $\text{SO}_2$  in the atmosphere being 2-7 days and 2-3 days respectively in eastern North America.

## 2.6. SOURCE-RECEPTOR RELATIONSHIPS FROM NUMERICAL MODELLING\*

2.6.1 Model Developments

The MOI modelling reports of 1982 were criticized in the following areas:

- (1) The simple statistical or trajectory models did not include non-linear aspects of atmospheric chemistry and wet scavenging.
- (2) The transport winds were treated simplistically ignoring vertical transport along frontal surfaces.
- (3) The topographical changes and the diurnal variability of the mixed layer were ignored, thus affecting the transport winds and dry deposition.
- (4) There was not sufficient data for an objective evaluation of the models to determine how well the models were able to reproduce reality.

Several Eulerian long range transport models (Canadian-German model, ADOM; EPA-NCAR model, RADM; Carmichael's model STEM I, II and III) have subsequently been developed to address points 1-3 outlined above. Also, the trajectory models have been more rigorously evaluated with improved input data and observed deposition fields. The conclusions of these studies are outlined in Tables 2.12 and 2.13. The main findings can be summarized as follows.

The simple trajectory models appear to simulate wet deposition of sulfur over a one year period reasonably well. This is because at this time scale the non-linear effects of atmospheric sulfur chemistry are not very critical (Table 2.12, Section 6). Several studies (Oppenheimer, 1984; Calvert (NAS, 1983)) have indicated that transformation of  $\text{SO}_2$  to  $\text{SO}_4^-$  may be approximated by a linear process. This may be attributed to the fact that the  $\text{SO}_2$  reaction with OH radicals in the dry phase is not a chain terminating reaction (Calvert (NAS, 1983)). Further, in the aqueous phase, the transformation of  $\text{SO}_2$  to  $\text{SO}_4^-$  is very rapid. This suggests that the formation of  $\text{SO}_4^-$  may be limited by the available  $\text{SO}_2$  rather than the oxidants away from high emissions areas. At an episodic scale, however, non-linear effects may be very important. (Table 2.12, Section 3b).

Although vertical motions are not explicitly treated in all trajectory models, some models (Ellenton et al., 1985; Johnson, 1983) parameterize the effects of wind shear and subgrid scale motion through a rate of growth along each trajectory. This indirectly accounts for the effects of

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\*Prepared by P.K. Misra, M.P. Olson and R.W. Shaw

vertical transport and vertical shear when model results are taken over long time periods (ie, one year). Vertical motions are treated as the third wind dimension in the trajectory models of Olson et al (1978) and Martin et al (1985). (Table 2.12, Section 2).

Because of the emerging evidence for long-term linearity and reasonable model annual simulations, there is reason to believe that the simple trajectory models can be used for source-receptor relationship studies for sulfur deposition. (Table 2.12, Section 7). However, extensive sensitivity studies and evaluation with observed data should be carried out to determine the uncertainties in model outputs. (Table 2.12, Section 5). For instance, most models use a single washout ratio to estimate wet deposition. However, Misra et al (1985) find the washout ratio to be extremely variable, spanning several orders of magnitude. It would thus be desirable to study the effects of randomly varying and functionally dependent washout ratios (Barrie, 1985) on the model outputs. (Table 2.12, Section 4). Similar arguments can be extended to other model parameters. Some of these studies are currently under way at many organizations, however, greater emphasis should be given to similar parameterization investigations.

Several, Eulerian models are currently operational as summarized in Table 2.13. A good data base is needed to evaluate these models. Past data bases, such as OSCAR or PEPE/NEROS, though useful, are not complete for an objective evaluation of these models.

#### 2.6.2 Model Applications

Can numerical models be used to estimate changes in deposition due to changes in emissions? This question is important because, if the answer is affirmative, atmospheric information can then be used to optimize, and thereby reduce, the cost of emission control strategies. There are two possible ways of assessing the results of control strategies: through the use of models, and the use of observations. Hidy (1984) has reviewed the advantages and limitations of quantifying source-receptor relationships through observations and models. In theory, observations from either routine or special monitoring programs could be used to estimate source-receptor relationships through the analysis of sulfur concentrations, the relative abundance of trace elements (receptor modelling) or special tracer compounds such as that used during the recent Cross-Appalachian Tracer Experiment (CAPTEX-83) or the proposed Massive Aerometric Tracer Experiment (MATEX). Hidy (1984) points out that using routine measurements of sulfur deposition and concentrations from operational networks still requires a model to interpret the results. The use of passive tracer releases and detection give insight only into the physical processes (transport and dispersion) affecting source-receptor relations. Analyzing observed concentrations during large, abrupt emissions changes during shutdowns or strikes may yield limited results because the emissions changes are often short-lived and the changes in concentrations and depositions due to the emissions changes are often masked by meteorological variability. Furthermore, deliberate emissions changes

Table 2.12 Recent developments in trajectory modelling

<u>TOPIC</u>	<u>RECENT INFORMATION</u>	<u>MODEL IMPLEMENTATION</u> <u>(TRAJECTORY MODELS)</u>	<u>REFERENCES</u>
<hr/>			
(1) <u>INPUT DATA</u>			
a) Emissions	<ul style="list-style-type: none"> <li>- Emission quality has improved with better information exchanges between EPS (Canada) and NAPAP (U.S.)</li> <li>- Better inventories of NO<sub>x</sub> and HC are now available</li> </ul>	<ul style="list-style-type: none"> <li>- Newer sulfur emissions reduce the uncertainty in this input</li> <li>- Nitrogen models will use these inventories</li> </ul>	Clark (1985) Toothman et al (1984) Bottenheim et al (1984) Shannon et al (1985)
b) Precipitation	<ul style="list-style-type: none"> <li>- Attempts to improve the temporal resolution of gridded precipitation analyses (from 24 to 6 hr) are being made</li> </ul>	<ul style="list-style-type: none"> <li>- An accepted high resolution precipitation field is not yet available. Individual modellers have attempted to improve the time resolution of precipitation, however this gives widely different deposition values.</li> </ul>	Samson et al (1985)
c) Mixing heights	<ul style="list-style-type: none"> <li>- Methods are available for deriving time varying mixing heights (from data or numerical weather prediction models)</li> </ul>	<ul style="list-style-type: none"> <li>- Not implemented in most trajectory models at this time only average or climatological mixing heights are used.</li> </ul>	Eliassen (1984)
<hr/>			
2) <u>TRANSPORT</u>	<ul style="list-style-type: none"> <li>- Tracer experiments are available to test trajectory models</li> <li>a) CAPTEX-83 b) NORTH SEA</li> <li>- Model studies indicate that either 925 mb or layer average trajectories are better than surface or 850 mb trajectories</li> </ul>	<ul style="list-style-type: none"> <li>- Tracer experiments have suggested model changes and these are being investigated.</li> </ul>	Summers et al (1985) Crabtree (1982) Fisher et al (1984) Clark et al (1984)  Viesmann (private communication)



Table 2.12 (Cont.)

<u>TOPIC</u>	<u>RECENT INFORMATION</u>	<u>MODEL IMPLEMENTATION</u> <u>(TRAJECTORY MODELS)</u>	<u>REFERENCES</u>
<u>3) TRANSFORMATION</u>			
a) In cloud chemistry	- Chemical transformation of SO <sub>2</sub> within clouds (ie aqueous chemistry) is very important.	- Not implemented in any of the trajectory models	Martin and Damschen (1981) Hegg and Hobbs (1981)
b) Linearity	- SO <sub>2</sub> transformation to SO <sub>4</sub> may be non-linear at episodic scales.  - Recent studies suggest that non-linearities between sulphur emissions and deposition are not large for long time and space scales	- Non-linear behaviour at episodic scales is not currently modelled  - This information suggests that in existing models, linear chemistry is a reasonable assumption for long term sulphur deposition.	Issac et al (1983)  Calvert (1983) Oppenheimer (1984)
<u>4) SCAVENGING</u>			
a) Dry Sulphur deposition	- New experimental data (eg, over forests and from "CORE" network) is becoming available - Spatial and temporal patterns over North America have been produced (SO <sub>2</sub> and NO <sub>2</sub> dry deposition)	- Not incorporated as yet  - ready for model testing	Den Hartog et al (1984) Hicks et al (1985)  Voldner et al (1985)
b) Wet Sulphur deposition	- Variability of washout ratios has been examined - log normal distributions and possible relationships with precipitation intensity have been noted. - The importance of in-cloud scavenging has received considerable attention in recent years.	- Some of these aspects of washout ratios are now being tested in Lagrangian trajectory models  - An Oversimplified parameterization has been implemented in some Lagrangian models, more complete in Eulerian models.	Barrie (1985) Misra et al (1985) Niemann (1982)  Banic et al (1985)

Table 2.12 (Cont.)

<u>TOPIC</u>	<u>RECENT INFORMATION</u>	<u>MODEL IMPLEMENTATION</u> <u>(TRAJECTORY MODELS)</u>	<u>REFERENCES</u>
5) <u>UNCERTAINTY</u>	<ul style="list-style-type: none"> <li>- Comparisons of Lagrangian model results with field data indicates that incorporated meteorology can explain approximately half of the variance in sulphur deposition.</li> <li>- An uncertainty workshop was held at Woods Hole in 1984. No readily applicable methodologies for assessing uncertainty were proposed.</li> </ul>	<ul style="list-style-type: none"> <li>- None of the models currently attempt to evaluate uncertainties in model results</li> </ul>	<ul style="list-style-type: none"> <li>Ellenton et al (1985)</li> <li>Eliassen et al (1985)</li> <li>Shannon et al (1985)</li> <li>Demerjian (1985)</li> </ul>
6) <u>EVALUATION</u>			
a) EMEP NATO-CCMS	<ul style="list-style-type: none"> <li>- European Lagrangian model evaluation found that models simulate annual sulphur concentration/deposition patterns reasonably well.</li> </ul>	<ul style="list-style-type: none"> <li>- Almost all the models simulate annual sulphur deposition reasonably well and some show good comparison with data on a monthly basis.</li> </ul>	<ul style="list-style-type: none"> <li>Eliassen (1984)</li> <li>Klug et al (1984)</li> </ul>
b) EPRI	<ul style="list-style-type: none"> <li>- U.S. Lagrangian model evaluation by SRI, Argonne and TRC.</li> </ul>	<ul style="list-style-type: none"> <li>- No analyses are available to demonstrate that the models would "work" as well when emissions are reduced significantly.</li> </ul>	<ul style="list-style-type: none"> <li>Bhumralkar et al (1985)</li> </ul>
c) ISDME	<ul style="list-style-type: none"> <li>As recommended by the MOI modelling subgroup. A study by AES/EPA to evaluate 11 models using 1980 data is in progress.</li> </ul>	<ul style="list-style-type: none"> <li>Seasonal and annual wet sulphur deposition vs. measured data for 1980 using descriptive statistics and spatial (pattern) comparisons.</li> </ul>	<ul style="list-style-type: none"> <li>Clark et al (1984-85)</li> <li>Voldner et al (1985)</li> </ul>

Table 2.12 (Cont.)

<u>TOPIC</u>	<u>RECENT INFORMATION</u>	<u>MODEL IMPLEMENTATION</u> <u>(TRAJECTORY MODELS)</u>	<u>REFERENCES</u>
<hr/>			
7. <u>SOURCE-RECEPTOR</u> <u>RELATIONSHIPS</u>			
a) Sulphur in Europe, N. America	The contribution of many source regions to receptor regions are shown in matrix (budget) form for Europe and N. America.	These matrices (budgets) are computed annually by linear Lagrangian models for use in transboundary analyses and control strategies.	Eliassen et al (1984) Bhumralkar et al (1982) MOI-2F-M (1982) Olson et al (1983) Johnson et al (1983) Samson et al (1985) Fay et al (1985)
	Intermodel agreement high on relative (ranking) basis.	Statistical intercomparison of MOI models matrices.	Voldner et al (1982)
b) Nitrogen	Computed for eastern North America	ASTRAP model modified for nitrogen chemistry with large uncertainty.	Shannon et al (1985)

Table 2.13 Recent developments in Eulerian Modelling

<u>TOPIC</u>	<u>RECENT INFORMATION</u>	<u>MODEL IMPLEMENTATION</u> (EULERIAN MODELS)	<u>REFERENCES</u>
1. <u>TRANSPORT</u>	Two basic methods for deriving transport winds are predictive numerical models and assimilation of observed data.		
a) <u>Predictive Models</u>	Existing weather prediction models or mesoscale models could be used to produce 3-D wind fields. The principle advantage of predictive models is that internally consistent fields can be produced (i.e. clouds, precipitation, the surface energy budget and the boundary layer structure are interrelated). The major problem with predictive models is that they can diverge from reality quite quickly (particularly predicted cloud or precipitation fields).	- The RADM transportation module uses a predictive mesoscale model originally developed at Penn. State. The model includes prognostic equations for cloud water and rainwater as well as boundary layer and surface energy models. To reduce model divergence from observations, reasonably frequent reinitialization is necessary.	Anthes and Warner (1978)  Hsie et al. (1984)
b) <u>Diagnostic Models</u>	To produce 3-D wind fields with the time resolution used in Eulerian models (1 hr) the objectively analysed data must be used in concert with prediction models. In this case the prediction model is used as a dynamic interpolator between two observation times.	- The ADOM model uses diagnostic input data. Analysed data go through the normal mode initialization procedures of the CMC weather forecast model to produce 3-D thermodynamic and dynamic fields. The CMC spectral model is used as a dynamic interpolator for this data. A combination of diagnostic and observed cloud and precipitation fields feed into a boundary layer/surface energy model.	Data System for TADAP/ADOM (1984)

Table 2.13 (Cont.)

<u>TOPIC</u>	<u>RECENT INFORMATION</u>	<u>MODEL IMPLEMENTATION</u> (EULERIAN MODELS)	<u>REFERENCES</u>
	The main advantage of this type of diagnostic data is that the 3-D wind field will correspond very well with the actual meso and synoptic scale flows.	If there are inconsistencies between the model cloud and precipitation fields and observed thermodynamic fields, the boundary layer structure can be affected.	
2. <u>CLOUDS PHYSICS AND SCAVENGING</u>			
a) CLOUD TYPES	- Because of differences in vertical transport, fractional coverage and microphysical properties, precipitation systems can be roughly divided into stratoform and convective types.	- Implementation of cloud processes in large Eulerian models (ADOM and RADM) is in a state of flux. - Some aspects are well developed at present but others will receive considerable attention in the future.	Region Acid Deposition (RADM) (1983) NADAP: Eulerian Model Development: Peer Review (1985)
1) Stratoform Cloud Models	- depends on vertical velocity ( $\sim 1$ to $10$ cm/s), moisture profile, cloud depth, temperature.	- ADOM model incorporates a simplified 1-D stratoform microphysical model using cloud base and thickness as input parameters. The model is driven by surface precipitation which determines the vertical velocity scale.  - RADM cloud models are under development but a separate stratoform model is not presently incorporated.	Rutledge (1984)  Karamchandani et al. (1985)

Table 2.13 (Cont.)

<u>TOPIC</u>	<u>RECENT INFORMATION</u>	<u>MODEL IMPLEMENTATION</u> (EULERIAN MODELS)	<u>REFERENCES</u>
ii) Convective Cloud Models	<ul style="list-style-type: none"> <li>- cloud vertical velocity (1-10 m/s) and fractional coverage yield cloud mass flux (ie convective transport)</li> <li>- temperature and moisture profiles then determine the cloud ensemble depth and microphysical properties.</li> </ul>	<ul style="list-style-type: none"> <li>- Although 1-D microphysical models are being considered they have not been implemented. This is a potential weakness of present Eulerian formulations.</li> <li>- both RADM and ADOM use parameterized convective formulations with convective transport dependent on surface precipitation.</li> </ul>	<p>Walcek (1985)</p> <p>Scire et al (1985)</p> <p>Scire and Venkatram (1985)</p>
b) WET SCAVENGING			
i)	Gases are scavenged via reversible exchange depending on the chemical concerned.	<ul style="list-style-type: none"> <li>-RADM calculates reversible gas-aqueous exchange assuming equilibrium conditions exist.</li> <li>-ADOM calculates reversible gas scavenging using a two film diffusion model for raindrops (for cloud droplets forward and backward rates from collision - sticking theory and Henry's law are determined).</li> </ul>	<p>Jacob and Hoffman (1983)</p> <p>Chameides (1984)</p>
ii)	Particles are scavenged via nucleation within clouds or collection in or below clouds. Particles can be released by evaporation.	<ul style="list-style-type: none"> <li>-both RADM and ADOM treat nucleation scavenging in a parameterized manner.</li> <li>-Collection scavenging by raindrops in ADOM is modelled using cloud microphysical formulations.</li> </ul>	

Table 2.13 (Cont.)

<u>TOPIC</u>	<u>RECENT INFORMATION</u>	<u>MODEL IMPLEMENTATION</u> (EULERIAN MODELS)	<u>REFERENCES</u>
c) FIELD STUDIES	-Designed to look at transport, microphysical, scavenging and chemical processes in clouds. EG (1) North Bay (2) U. of Washington (3) Brookhaven National Laboratory	-Evaporation (or any exchange between cloud water reservoirs) results in a pollutant mass exchange proportional to (transformation rate) (size of reservoir)  -Feedback from such field studies have as yet not been implemented in large Eulerian models.	Isaac et al. (1984) Leaitch et al. (1985) Isaac and Daum (1985) Hegg et al. (1984) Duam et al. (1984)
3. <u>CHEMISTRY MECHANISMS</u>			
a) Gas-phase	A large number of interrelated chemical reactions have been found to affect gas phase oxidation of $\text{SO}_x$ and $\text{NO}_x$ . These reaction chains include both inorganic and organic species. Good quality information exists about many of these gas phase reaction rates. (Chemical reaction mechanism table available on request).	-The RADM model includes 80 chemical reactions while ADOM contains 112 reactions which affect sulfur and nitrogen chemistry. -The two models treat inorganic chemistry in a similar manner but significant differences in the mechanism are exhibited in the treatment of organic species. -Both gas phase chemical mechanisms have been verified against smog chamber data.	Lurm et al (1985) Stockwell et al (1985)

Table 2.13 (Cont.)

TOPIC	RECENT INFORMATION	MODEL IMPLEMENTATION (EULERIAN MODELS)	REFERENCES
b) Aqueous Phase	<p>Clouds are recognized to perform a role in the transformation of <math>\text{SO}_x</math> and <math>\text{NO}_x</math> to sulfate and nitrate. Knowledge of the important chemical reactions within cloud water and precipitation elements and the overall chemical transformation rates for sulfate and nitrate is progressing. Some tentative conclusions about <math>\text{SO}_2</math> oxidation are:</p> <ol style="list-style-type: none"> <li>1) <math>\text{H}_2\text{O}_2</math> oxidation dominates at <math>\text{pH} &lt; 4.3</math>.</li> <li>2) <math>\text{O}_3</math> is significant at higher pH.</li> <li>3) Fe and Mn can be important catalysts in heavy industrial areas during winter.</li> <li>4) Organics such as formaldehyde can be form complexes with <math>\text{SO}_2</math> and inhibit <math>\text{SO}_2</math> oxidation. However, this does not appear to be a significant problem.</li> <li>5) Most <math>\text{H}_2\text{O}_2</math> is gas-phase produced. However, this will depend on the sticking coefficients of OH and <math>\text{HO}_2</math> radicals.</li> <li>6) <math>\text{NO}_x</math> aqueous phase chemistry is not considered to be very important. Most <math>\text{NO}_3</math> is gas produced.</li> <li>7) <math>\text{SO}_4/\text{NO}_3</math> ratio in cloud water is high suggesting most acidity to be <math>\text{SO}_4</math> related.</li> <li>8) Acid neutralizing substances such as <math>\text{NH}_3</math>, Ca etc. affect mass transfer to cloud and rain water and hence oxidation.</li> </ol>	<p>-The ADOM and RADM models include 20 to 40 aqueous phase chemical reactions (including gas-aqueous phase exchanges). ADOM includes both a convective and a stratoform model containing the more detailed aqueous phase mechanism. Development is continuing on these aqueous modules as more is learned about the subject.</p>	<p>Daum et al (1984) Graedel et al (1981) Schwartz (1984) Karamchandani et al (1985) Scire and Venkatram (1985) Walcek (1985)</p>



Table 2.13 (Cont.)

<u>TOPIC</u>	<u>RECENT INFORMATION</u>	<u>MODEL IMPLEMENTATION</u> (EULERIAN MODELS)	<u>REFERENCES</u>
4. <u>DATA NEEDS AND EVALUATION</u>	<p>Comprehensive Eulerian models need a large data set for evaluation. Priority data sets needed for model initialization and evaluation have been identified.</p> <p>The existing data sets, such as OSCAR and PEPE/NEROS are not adequate for a thorough model evaluation. The methods to evaluate these models are expected to be complex.</p>	<p>Partial evaluations with the OSCAR data set have been conducted for ADOM and RADM.</p> <p>A more comprehensive data set acquisition is being planned. Studies such as PRECP and STORM are underway. The data from these studies will be useful for process studies. Several model evaluation techniques are under review.</p>	<p>Christie (1985)</p> <ol style="list-style-type: none"> <li>1. OSCAR</li> <li>2. PEPE/MEROS</li> <li>3. MATEX</li> <li>4. COMPEX</li> <li>5. CANADA/US</li> </ol> <p>Joint field study concept plan</p> <ol style="list-style-type: none"> <li>6. PRECP</li> <li>7. STORM</li> </ol>

(modulation) can be socially disruptive. Finally, deliberate tracer releases or emissions changes at a limited number of locations give, in any event, atmospheric linkages for only those sources.

Hidy (1984) concludes, therefore, that estimates from properly verified models may be more useful in estimating source-receptor relationships than field measurements of sulfur concentrations and deposition. Indeed, most of the effort that has gone into establishing source-receptor relationships has been through the use of models because of their potential ability to estimate the relative contribution of many different source regions to concentrations and deposition at a large number of receptor points. Properly verified models can be used to indicate where emission reductions could be most effectively applied to reduce concentrations or depositions at sensitive ecosystems. Long range transport (LRT) models usually express source-receptor relationships in terms of "atmospheric transfer matrices" which list the concentration or deposition at a given receptor point per unit emission in a given source region (Olson, 1983; MOI, 2F-M, 1982).

Source-receptor matrices have been a very popular tool in developing source abatement strategies in North America and Europe (Alcamo, 1984; Fortin, 1983; Streets, 1983, 1984; Young, 1985; Shaw, 1983, 1985; Oppenheimer, 1983, 1984; Hidy, 1984; Ellis, 1985; Fay, 1985). Methodologies range from simple overall linear reductions of 50%, based on target loadings which are approximately one-half the annual maximum measured sulfur deposition, to targeted strategies, which use transfer matrices to identify the largest emission regions contributing to the deposition at the receptor sites and proceed to reduce the emissions in these regions until target limits are reached at the receptors. Other approaches involve more emissions regions with smaller reductions per region such that emission reduction costs are minimized. The cost-benefit functions can be quite controversial but they are important to formulate and incorporate into the system. Lacking evidence of strong non-linearity in the acid deposition processes on a regional and annual scale, all current approaches recognize the linearity inherent in the abatement strategy methodology. The methods can incorporate the effect of background pollution which cannot be readily changed but which does contribute significantly to some remote receptors.

Although these abatement methods, or variations of them, can predict that given changes in emissions in certain regions will result in given deposition changes at certain receptors including associated cost estimates, the detection or measurement of these changes may not be readily evident at the receptors, due to the natural variability in meteorological and atmospheric processes, unless the changes are sizable or the measurements are continued carefully for many years. Current information suggests that these changes on long time/space scales will occur in an approximately linear fashion.

Although the question has by no means been finally resolved, there is a growing consensus among scientists, including those attending the recent

International Symposium on Acidic Precipitation, held at Muskoka, Ontario on 15-20 September 1985, that the present LRT models are capable of at least indicating the relative merits of various long-term control strategy options, especially if sources are aggregated over broad geographical regions (Hidy 1985, Young and Shaw 1985).

It is very important, however, that the LRT models be carefully used with full recognition of the severe limitations which they still possess and which will be briefly discussed below. As Summers (1984) and Young and Shaw (1985) point out, the present LRT models are best used in a qualitative sense for ranking the various source regions in terms of relative (rather than absolute) contribution to deposition and, therefore, for weighing the relative merits of various control options. They are not yet likely to give a very precise estimate of the reduced depositions resulting from control measures, although they appear to be presently capable of estimating sulfur deposition, averaged over at least several seasons or a year, to within a factor two or better of observations (Ley et al 1985; Eliassen and Saltbones, 1983 and 1985; Endlich et al 1984; Kleinman 1984; Fisher 1983; Gisason and Prahm, 1983; Ellenton, 1985; Eliassen, 1984; Knudson, 1983; Voldner, 1981, 1983; Klug, 1984; MOI 2F-M, 1982).

Models are less successful at estimating deposition over shorter periods, especially because of meteorological variability. Samson (1985) and Shannon (1985) state that meteorological variability precludes using LRT models at the present time for developing detailed individual source-by-source emission control strategies.

Most of the present models are linear in nature; i.e. they assume that changes in concentrations and deposition are proportional to changes in emission rates. Because of the complex chemical interaction of the precursors for both atmospheric acids and the oxidants producing the acids, the atmospheric chemistry is almost certainly not linear. Shaw and Young (1983), using a relatively simple chemical model, concluded that the errors caused by non-linearity on predictions of concentrations are not large, while Oppenheimer (1983) using a climatological box model concluded that uniform SO<sub>2</sub> emission reductions in the eastern United States will produce a nearly proportional reduction in wet sulfate deposition originating in those emissions and deposited on land areas. It is obvious that, if a large enough geographical area is considered, the total sulfur chemistry must be linear because what goes up must eventually come down. The uncertainty lies with the time and space scales over which linearity is a reasonable assumption. On an episodic scale, the relationship between emissions and wet deposition is likely to be non-linear. These effects have been demonstrated by Eulerian model runs and some data analysis. The variability introduced by episodicity cannot be fully represented by the Lagrangian models. It is anticipated that the complex Eulerian model being developed jointly by the Canadian, Ontario and West German governments (Venkatram et al, 1985), may place bounds on the validity of the linearity assumption.

In summary, the consensus among scientists is that, despite the many unresolved problems in their treatments of the physical and in particular the chemical processes affecting LRT, and the need for greater model assessment, LRT models are at the present time capable of assessing the relative merits of various control options that deal with large source regions (of the size of a state or province or group of states) and periods of at least a year or several years. The extrapolation of these linear source-receptor relationships into future meteorological regimes and different emission distributions, while they can provide a best guess or first estimate, could result in some locally unexpected deposition changes so that long-term monitoring will be required to detect the anticipated overall deposition trends.

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Assessment of the state of  
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